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TECHNICAL MEMORANDUM

NO. 3

ULTRASONIC PROPAGATION IN LIQUIDS UNDER HIGH PRESSURES

BY

G. J. HOLTON

DECEMBER 1, 1948

ACOUSTICS RESEARCH LABORATORY

DEPT. OF ENGINEERING SCIENCES AND APPLIED PHYSICS

HARVARD UNIVERSITY - CAMBRIDGE, MASSACHUSETTS

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Department of Engineering Sciences and Applied Physics

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Abstract

The problem under discussion is the velocity and attenuation of ultrasonics in liquids at various temperatures and high pressures. This report deals with the development of the apparatus and the method of measurement, the data obtained therewith, and a brief theoretical treatment of the data.

The electrical apparatus makes use of a presentation unit (Loran receiver or A/R 'scope) which synchronizes the sequence of operations by internally generated trigger signals at low repetition rates. Three- to five-microsecond pulses at controllable amplitude and approximately 15 Mc/s carrier frequency are imposed on an X-cut quartz crystal which has been placed inside a pressure-supporting vessel containing the test sample. The resulting ultrasonic pulses in the liquid are reflected back and forth over a definite path-length between the transducer and a mirror. After amplification in a receiver strip with calibrated gain control the complete echo-pattern becomes available for visual comparison on the presentation screen. The timed relative delay and the measurable amplitude differences between successive pulses furnish data for velocity and attenuation measurements when certain corrections are attended to. The sources of error are discussed in detail for both types of measurement.

Numerical data for the velocity in water as a function of pressure to about 6000 atmospheres are presented at temperatures between 25 and 50°C. Velocity data for toluene and ethyl ether are also given and compared with earlier measurements by other methods which covered a much smaller pressure range.

From the data on water, information is derived on the temperature coefficient of sound velocity and on the ratio of specific heats at increasing pressures. The latter results are compared with those obtained directly from purely static

experiments, and the advantages of the ultrasonic measurement technique for the derivation of some of the thermodynamic coefficients are cited.

The attenuation measurements for water yield a linear law relating the critical pressures and temperatures at which the well-known anomalous or nonclassical part of the sound attenuation becomes negligible. The theoretical discussion of these attenuation curves leads to a correlation between the degree of association of the liquid and the excess attenuation. Comparison with the results of other theories is made which gives support to the conclusion that the classical attenuation formula has to be amended to account for attenuation in the non-ideal, associated liquid.

Attenuation measurements are reported also on ether and toluene. Recommendations are made for further development and research, particularly with a view to elimination of residual errors which prevent the use of these tools for <u>absolute</u> measurements. A fairly comprehensive bibliography of this subject is given, which includes instrumentation, measurements and theory. (Contracts abroad)

Ultrasonic Propagation in Liquids under High Pressures

by

G. J. Holton

Acoustics Research Laboratory

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I

Introduction

The research problem with which this report is concerned was, to a large extent, made possible only by the recent development of precision methods for measuring short time-intervals between signals of a few microseconds' duration having a carrier frequency in the ultrasonic range. The equipment involved, and the "multiple-echo" method for determining the velocity and attenuation of sound which was developed with it, will not be unfamiliar to those acquainted with Loran and Radar trainers, and with devices for detecting flaws in metals by means of ultrasonics. A useful bibliography of other adaptations of the echo method will be found in (82).*

The problem for which the new tools were used here are these:

1. The measurement of sound velocity as a function of temperature and pressure in a sample of liquid material.

2. The use of such data to compute, in conjunction with independently available static p-v-T measurements, such thermodynamic coefficients as the ratio of the specific

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*See Bibliography at the end of the report.

heats.

3. The measurement of sound attenuation constants.

4. The interpretation of these data in the light of theories of the structure of liquids.

5. Preparation for velocity and attenuation studies on solids.

Work on the velocity and attenuation of sound has been going on widely and vigorously, especially during the past ten or twenty years; but very little attention has been directed toward the higher pressure range. In particular, the question of the association of water molecules at ordinary pressures and temperatures seemed to call for experimental work in a wider temperature and pressure range.

Accordingly, the experimental apparatus was assembled, an adequate measurement technique was devised, and data were taken on water and other liquids to about 6000 kg/cm^2 and between 25°C and 50°C. Work under the first four headings listed above was carried to a point where further improvements in technique and results could be gained only by an uneconomically large expenditure of time and effort - the point where a satisfactory routine method for gathering further data on liquids was finally available and where, at the same time, the projected extension of these measurements to solids seemed possible. This report extends up to that particular stage.

II

Previous Application of Sound Measurements at High Pressures

The literature on previous experiments on sound at high pressures, though scant, did reveal some of the technical difficulties to be expected. Swanson[140-142] in 1934 had measured the pressure coefficient of sound velocity, $(\partial u/\partial p)_T$, for nine organic liquids to 300 atmospheres at room temperature. Using an interferometer technique developed by Hubbard and Loomis,[77] he claimed an accuracy of 1 in 1000 for his velocity data. This figure is generally considered to be the best accuracy reasonably obtainable unless extraordinary labor is put into design and secondary measurements.* Like most other early investigators in this field, Swanson did not go to the trouble of providing either for measurements in electrically conducting liquids or even for thermostating of the sample liquid. His measurement technique consisted of moving a sound mirror to and fro in relation to a stationary transducer which generated continuous 200 kc/s sound waves, and noting the change in the electrical loading reflected into the driving circuit by the alteration of the acoustic impedance in front of the transducer. Although this method has since been extensively refined to yield both velocity and attenuation measurements, it is not to be recommended at higher frequencies and higher pressures; for example, the packing around the rod which guides the round mirror is likely to leak.

The results in his very limited pressure range showed a practically linear increase of velocity with rising pressure

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*Cf. Schreuer's precision work (131).

for all liquids tested. This change is particularly large in ethyl ether and pentane, where 1000 atmospheres of applied pressure would seem to threaten an increase of velocity by a factor of 2. This was important information for the design of the spacer distance in our own measurement cartridge, as will be seen.

Another of Swanson's difficulties was to beset this research as well: His absolute velocity values, when extrapolated to zero additional pressure, did not quite coincide with independently established values at these conditions of pressure and temperature; the deviation reached as high as 1 per cent for some of his liquids. Swanson ascribed this failure to impurities in the liquids, and although no other evidence of impurities was found in our measurements, the explanation may also hold for this work. The worst such discrepancy observed in our research was one deviation of +2.5 parts in 10,000 from the likely value of the velocity in water at 50°C (see p. 43). This error is on the verge of the limits of accuracy of both the standard values and our own measurement, and is consequently not serious; but the positive sign of the discrepancy is at any rate expected to result from an impurity.*

Swanson also warned of another problem to be expected in this work: "The correlation between the calculated and experimental values [of velocity] is not as good as we had expected. However, considering the uncertainty of the values of many of the thermodynamic coefficients used in the computations, they are in very good agreement. In some instances the values given by different observers varied as much as 20 per cent!"** The disagreement here mentioned actually reaches 10 per cent for some of his liquids around 250 atmospheres, and points to

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*Cf. Willard (154) p. 238.

**Reference (141) p. 692.

even poorer correlations at higher pressures.

An original but somewhat crude method of velocity measurement in liquids under pressure is given by A. C. Talbott.[143] Pressure pulses are generated by squirting a small quantity of liquid into the full pressure chamber. The incidence of the pulse as well as of subsequent echoes is recorded photographically by means of a mirror-and-lever system connected to a terminating membrane at one end of the chamber. The most obvious limitation is the pressure range, which is less than 425 kg/cm^2 in his model.

Some experimental work on gases to 100 atmospheres' pressure was done by A. H. Hodge[70] in 1937. An interferometer similar to Swanson's was used, and it permitted him and J. C. Hubbard[75] to calculate values of α to several tenths of a per cent. Hodge found an alarming 0.011 per cent increase in the resonance frequency per atmosphere of pressure. This would indeed have resulted in a serious shift in frequency for pressures as large as our projected 12,000 kg/cm^2; but it appears that this shift applies only to his particular regenerating circuits in which the transducer itself is used as coupling element, and/or in experiments where the transducer element is exposed to gases under pressure. At any rate, no such increase was found in our experiments, though provision for some adjustment had been made in the design of the driving circuits.

Hodge's interferometer technique, like Swanson's modification, required the calibrated motion of a rod passing out of the pressure chamber through a packing box. Attempts to overcome the difficulties inherent in such a design are found in the only other publications on research on sound under pressure, those by Biquard and by Bancroft. P. Biquard[16-19] made measurements of velocity for several liquids and the only known attenuation measurements (for toluene) of about 7- and 10-Mc/s

sound at ambient temperatures to 800 kg/cm^2. Since it uses diffraction of light by the density-grating set up by the traveling sound waves, this method too has its own obvious limitations. One or two thousand atmospheres might well be the maximum pressure which the essential glass windows in Biquard's arrangement can be expected to endure; below this point the optical method (originated independently by Debye and Sears as well as by Lucas and Biquard) may be brought to such perfection that the most accurate absolute velocity values for transparent media can be obtained with it.*

In Biquard's work the temperature fluctuated badly during some of the runs, and may have been greater inside the test chamber where continuous operation of the transducer may cause substantial heating of the sample in contact with it.** Further, the plotting of at least one of Biquard's curves (for the velocity of water at 16°C) is open to dispute. Except for this one curve, however, agreement with corresponding data in Swanson's publication and in this paper does occur within the expected error limits.

In 1939, D. Bancroft[3] investigated the velocity of sound in nitrogen at pressures to 9000 atmospheres. A resonance method was used, the change of sonic path in terms of wavelengths between his Rochelle salt transducer and microphone being accomplished by a change of frequency of the continuous sound waves. This dispenses with a rod passing through a packing.

The values of specific heats could be calculated to within 2 per cent. But though this method may seem attractive, it is not convenient for attenuation measurements and is unsuitable

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*Cf. References 131, 132.

**This point can be raised against most investigations not using short low-power pulses with the exception of Schreuer's.

with quartz crystals in the ultrasonic frequency range of interest here. Nevertheless, Bancroft's work is particularly valuable to us because of his attention to errors; significantly, the source of his most bothersome error, the parasitic resonance of the container, is fortunately ruled out in our pulse method by its very nature.

This survey of earlier methods helped to emphasize the advantages inherent in the suggested velocity and attenuation measurements by timing and by comparing amplitudes of successive echoes over a known path. These advantages may be summarized as follows:

1. Both sets of required data are immediately and simultaneously available, and few secondary experiments are needed for their reduction.

2. The error corrections, though numerous, are much more easily handled in this procedure than, for example, in resonance methods involving parasitic resonances.

3. The echo method does not depend on precision measurements of changes of distances inside the pressure chamber, and so dispenses with the necessity for rods passing through packings.

4. Large power outputs can be expected from the quartz transducer during the short interval of its operation; and even under such conditions the heat losses per second at the crystal are negligible for low repetition rates.

5. Under favorable conditions, one may expect velocity measurements as accurate as those obtained by almost any other method and attenuation measurements superior to most other methods.

6. No other method seems so ideally suited to prospective work on solids, of which this investigation is a preliminary phase.

III

Apparatus

In principle, the apparatus used in these experiments operates not very differently from a radar set, with ultrasonic pulses at about 15 Mc/s and of a few microseconds' duration taking the place of electromagnetic pulses. The transducer, used as sender and receiver, is a small X-cut quartz crystal disk being driven at its fundamental frequency. The power pulse, or "main bang," can be of considerable strength because for such brief applications the voltage difference between the faces of the 15 Mc/s crystal can be more than 5000 volts. The acoustic radiation, released at intervals of many thousand microseconds, is directed down a tube containing the liquid under investigation, and is reflected back toward the crystal from an optically flat steel disk at a convenient fixed distance. If care is taken to provide a good mismatch at the two ends of the sonic path, a great number of multiple echoes will reach the crystal following upon a single power pulse. These echoes arrive at a measurable rate depending on the length of the sonic path and the velocity in the medium, and with a measurable decrement depending, at least in part, on the attenuation constant of the liquid. The transducer, tube, and contained liquid (an assembly called "the cartridge") are immersed in a pressure-communicating fluid. Over a single electrical lead to the external electronic equipment, data on time per echo and decrement per echo under various conditions of temperature and pressure are received simultaneously.

Timing Chain and Presentation Unit

The electronic equipment is the time-keeping heart of the method, and deserves special comment since, so far as is known,

the arrangement is in many respects unique. It is, moreover, adaptable to numerous other uses.

After considerable but fruitless effort to stabilize an Airborne Loran model sufficiently for the purpose, a Shipboard model DAS Loran set was remodeled to serve as the timing chain. The DAS provides the trigger pulses (at the rate of one every 0.02 second) for the "main bang" from the transmitter, as well as the presentation unit for the echoes received by the transducer, i.e., the mechanism for timing echo intervals and comparing echo amplitudes. These functions are synchronized by a 100 kc/s crystal from which coded "markers" at 500, 50, 10 and 2 μsec are derived for superposition on the echo pattern - a set of brief, evenly spaced excursions of the trace on the cathode-ray tube screen. Instead of reading off directly the time elapsing between the first and last echo, accuracy of measurement is improved by using the trace of the 'scope in two sections, one above the other. Each half of the trace lasts 0.02 second, so that the complete echo patterm is presented on each half. On the screen, it is possible to present simultaneously (1) an interval of about 50 μsec of sweep (with echoes and markers), in the neighborhood of the main bang, on the first half of the trace; and, superposed on this, (2) a selected 50-μsec portion of the second part of the trace. It is accordingly possible to "match up" the first echo on the first, or upper, half-trace with, say, the 50th echo on the second half-trace. The consequent displacement of the set of coded time-markers on one half-trace with respect to the other can (with a little practice) be read off in terms of microseconds, more or less as one might read a slide rule if its numerical symbols were missing.

The time elapsed per echo is obtainable at once by dividing by (n-1) the observed delay between the first echo on the upper and the n^{th} echo on the lower trace. This presupposes sufficient stability in the set to insure accurately timed

triggering of successive main bangs, as well as dependable behavior of the successive half-traces.

Much work on the Loran set was needed at this point, including the insertion of decoupling networks, careful matching of tubes, provision for constant line voltages, and frequent and accurate alignment of the timing chain. This latter precaution was most important since the sweep circuits had been modified to give a maximum "enlargement" of about 50 μsec per half-trace instead of the provided maximum of 160. The modification increased the accuracy to between 1/2 and 1 μsec per reading, which usually meant 1 to 2 parts in 1000 on velocity data. It is very likely that greater accuracy could be obtained by a complete redesign of the existing sweep circuits. At present they seem to rely too heavily on extreme economy of parts (understandable in a 43-tube set) at the expense of stability at the high sweep speeds.

From these measurements of time intervals per echo, the relative velocities of sound with changing conditions are obtained simply enough. In principle, at least, the measurement of attenuation of sound in the liquid is similarly straightforward. In our previous example the first and 50th echoes were "matched up" to obtain the time delay between them; unless all sources of attenuation are negligible (a situation to be expected only in some solids), the 50th echo will show much less amplitude than the first, and the difference in height of the two patterns on the screen could be calibrated in terms of loss (in decibels) of sonic pressure. Actually, it is far more accurate for both kinds of measurements to match pulse pictures of <u>equal</u> amplitudes, and a calibrated gain control has accordingly been constructed and incorporated into the amplifier and detector that communicate the echo pulses from the transducer to the presentation unit. An additional requirement was a "balance" control to permit a calibrated increase of amplification of the incoming echoes <u>only</u> during the period correspond-

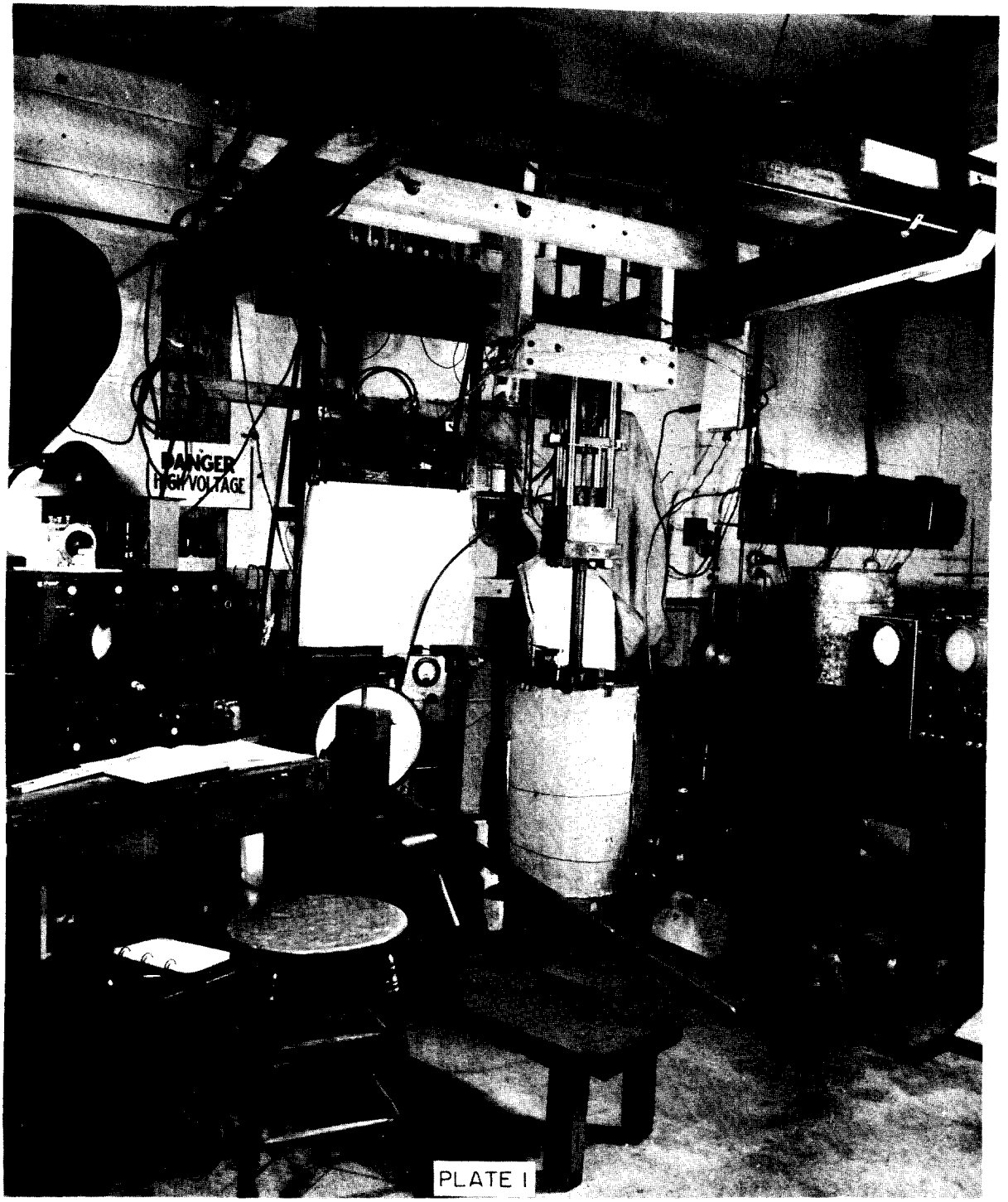

PLATE I

ing to the presentation of the second and variable half-trace. With this method, achieved by feeding a selected blanking pulse to the receiver during the half-duty-cycle corresponding to the upper trace, differences between echoes could be fixed immediately to ± 1/4 db by the turning of two dials.

The total attenuation per echo evidently is the relative attenuation between the n^{th} and m^{th} echoes in decibels, divided by (n-m). The true attenuation in the liquid (in db/echo or db/cm or cm^{-1})* is obtained after corrections have been made for the various other losses (resulting from beam spreading, imperfect reflection, etc.) which the sound beam undergoes. The assumptions behind this simple suggestion are fairly serious and had to be checked with care. The magnitude of the corrections in attenuation measurements, their dependence on the distance traveled by the sound, etc., are more difficult to determine than corrections relating to the velocity of sound. The details are given in the sections on errors later in this report.

Pulser or Driver

Figure 1 is a schematic diagram of the relation between the various components in the whole assembly. The original trigger pulse is an extremely short square pulse taken from the Loran time chain at a point where the additional loading creates no noticeable instability. As already mentioned, the repetition rate is 0.02 second. A variable trigger delay of 1000 to 3000 μsec is interposed between timing chain and pulse generator, since the trigger coincides with the beginning of each half-trace and the portions of the sweep which can be selected and expanded occur about 2500 μsec further along the trace. This delay circuit and the trigger amplifier were built

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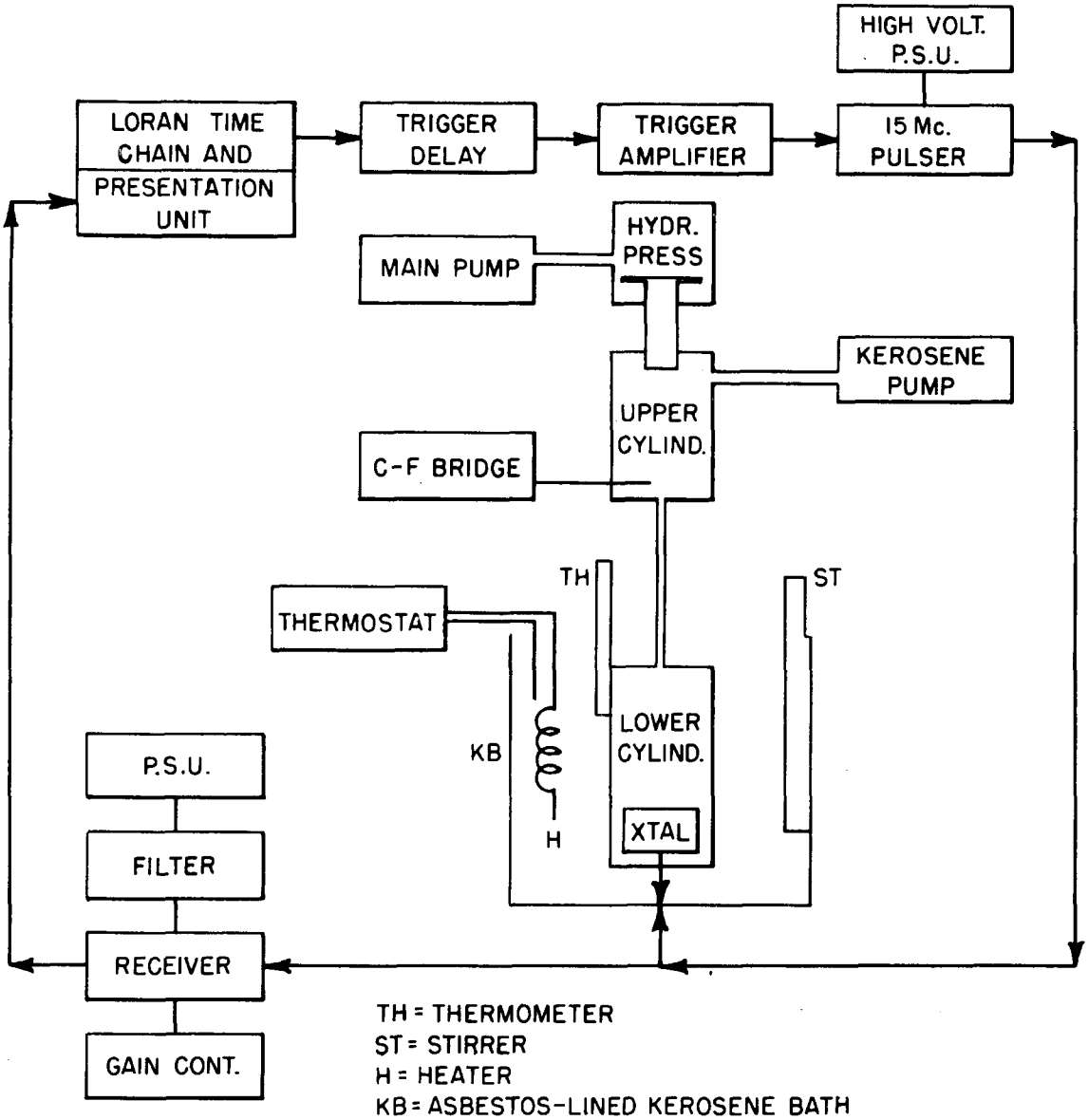
* Note: attenuation in db/cm = 8.7 x attenuation in cm^{-1}.

on the model of such standard circuits as the fixed A-pedestal delay in the DAS.

At the output of the amplifier we obtain a strong negative signal, a few microseconds long, with fairly steep sides and at the same repetition rate mentioned above. (If an A/R 'scope is used in place of the Loran set, the trigger, at desired repetition rates, is supplied directly to the pulser.)

The pulser whose design parallels that of the more recent ultrasonic radar trainer circuits, is essentially a shock-excited oscillator. The trigger serves to cut out momentarily an a-c ground across a Hartley oscillator tunable around 15 Mc/s by means of a composite-core coil. The length of the effective oscillation cycle may be controlled at the input point by adjusting the trigger pulse and/or by changing the bias on the "a-c ground" tube. In our method of matching echoes rather than finding a reference point on the leading edge of a single echo [113] it is not important to work with very fast rise-times. Even so, the leading edge of the r-f pulse rises to the half-power point within a few tenths of a microsecond. The trailing edge is spoiled in any case by the "ringing" of the crystal.[33]

The r-f pulse is amplified before application to the crystal by an 829 power amplifier whose variable plate voltage is derived from a separately constructed high-voltage power supply unit. There is a matching network in the output to the line; the 75-ohm coaxial cable to the crystal in the cartridge is kept as short as possible. This is one of the points brought out by Plate 1, which is a photograph of the laboratory including almost all components appearing in Fig. 1. The large rack left of center contains the pulser at about half-height. The large circular drum to its immediate right contains the temperature bath, the pressure chamber, and therefore the crystal transducer itself.



SCHEMATIC DIAGRAM OF ELECTRIC AND MECHANICAL LAY-OUT

FIG. 1

Crystal and Cartridge

The need for a matching network at the crystal has been pointed out at length in previous publications dealing with delay lines[12,78] and other devices using single echoes.[33,113] But in the multiple-echo method, the matching network is dispensed with, though this may make the electric power output at the pulser seem excessively high for a given acoustic input into the liquid. On the other hand, the pulser can supply far more power than the liquid can accept without serious anomalies in attenuation and velocity. In fact, this mismatch loss is not significant even in liquids with high attenuation constants, though the measured capacitance across the crystal may seem astonishingly high. The crystal capacitance itself can be computed to be only 15 μμf, but the stray capacitance is over 100 μμf, most of which is unavoidable in the present standard design of the terminating plug for the pressure chamber housing the coaxial cable to the crystal.

Some thought had to be given to the Q of the crystal transducer. It would seem to be desirable to keep it as low as possible, if only to obtain faithful reproduction of impressed pulses and some possibility of slight frequency adjustment. In vacuo the 15 Mc/s disks used in this work can be expected to have a Q of the order of 10^4, but the loading on both crystal faces in the cartridge reduces this figure considerably. Exact calculations at this point are difficult because the boundary conditions (clamping, etc.) cannot be determined accurately. However, for the ideal case of an unclamped crystal loaded on both faces by liquids, with an acoustic impedance like that of water, the Q is of the order of 10. This result also applies to other conditions of loading as long as the impedance match between the quartz material and the damping materials is not too poor.

A Q of 10 is not unsatisfactory as far as operating bandwidth is concerned; the available range of 1.5 Mc/s between

half-power points should be sufficient for the small frequency adjustments that might be required. Moreover, from the point of view of "ringing," i.e., persistence of oscillation after cessation of the applied power pulse, this value is not too high if the applied power pulse is sufficiently short compared to the time of travel per echo. At high velocities (that is, high hydrostatic pressures) and for poorly chosen mirror-crystal distances, the tail-end of the outgoing pulse may beat with the leading part of the returning echo, and so distort it. Indirectly, therefore, this factor controls the determination of the shortest distance between mirror and crystal that may be considered for a given liquid. This distance in turn determines the upper limit of attenuation constants that may be measured with accuracy.

The very real danger of pulse distortion due to high Q was experimentally shown when a 5 Mc/s crystal, driven at the third harmonic, was substituted temporarily for the 15 Mc/s unit. The 5 Mc/s crystal has a Q three times larger than the thinner disk, other things being equal, and the echo-shapes for short sonic paths in water actually did indicate this change for the worse. All subsequent measurements were accordingly made with 15 Mc/s crystals (even though they are only 0.075 inch thick and very fragile*).

Before continuing to follow the path of the pulses (after reflection) through the receiver and back to the presentation unit, a thorough discussion of the cartridge assembly is called for. From a purely mechanical point of view, this part involved

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*Though the crystals allegedly had been cut to 15.0 Mc/s by the commercial supplier, in actual operation best results were obtained at about 14.8 Mc/s. This difference was of no consequence since allowance in the pulser networks had been made for such a shift, and since the receiver had ample bandwidth. Further specifications of the crystals follow approximately those in Ref. (127).

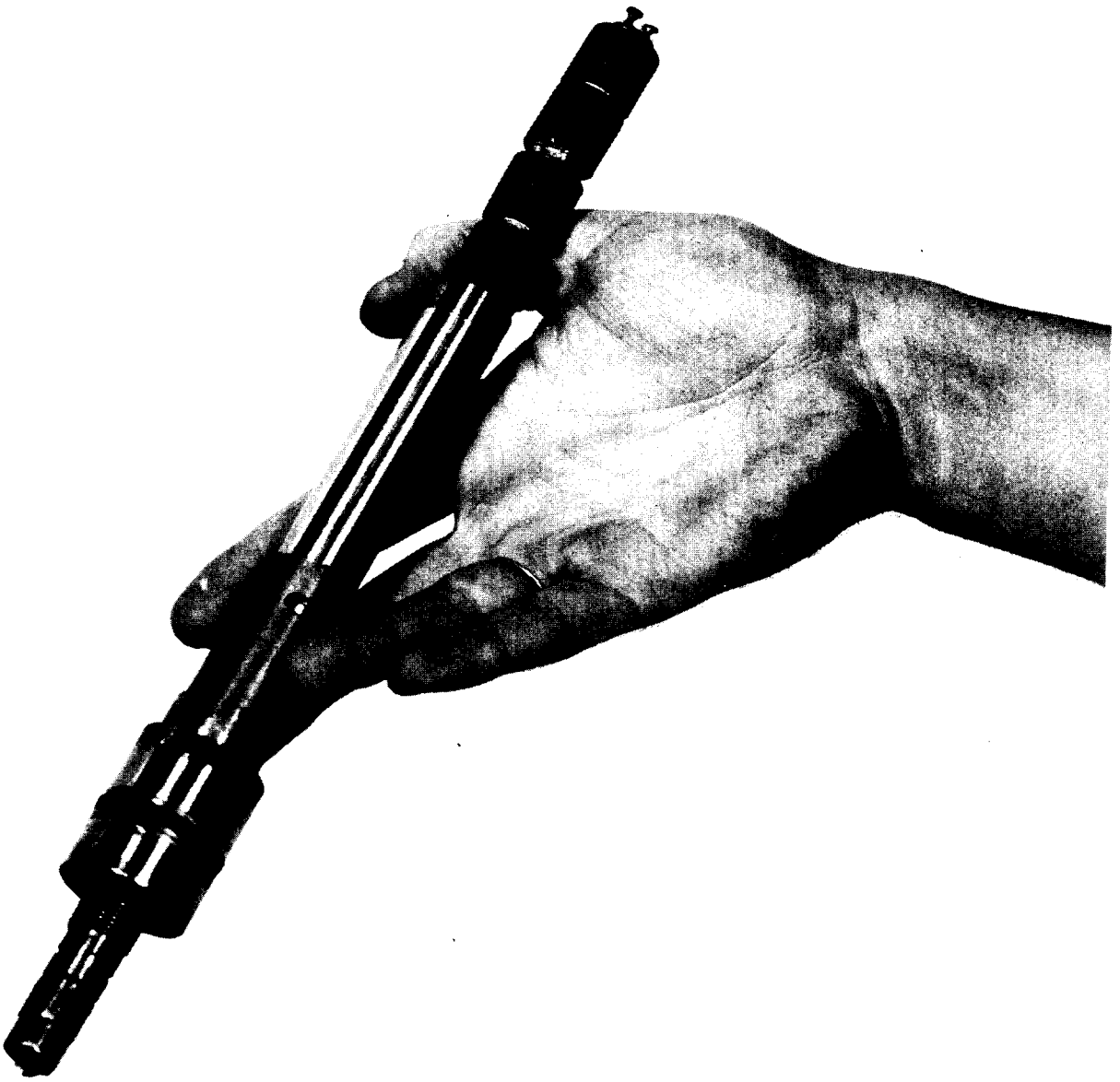
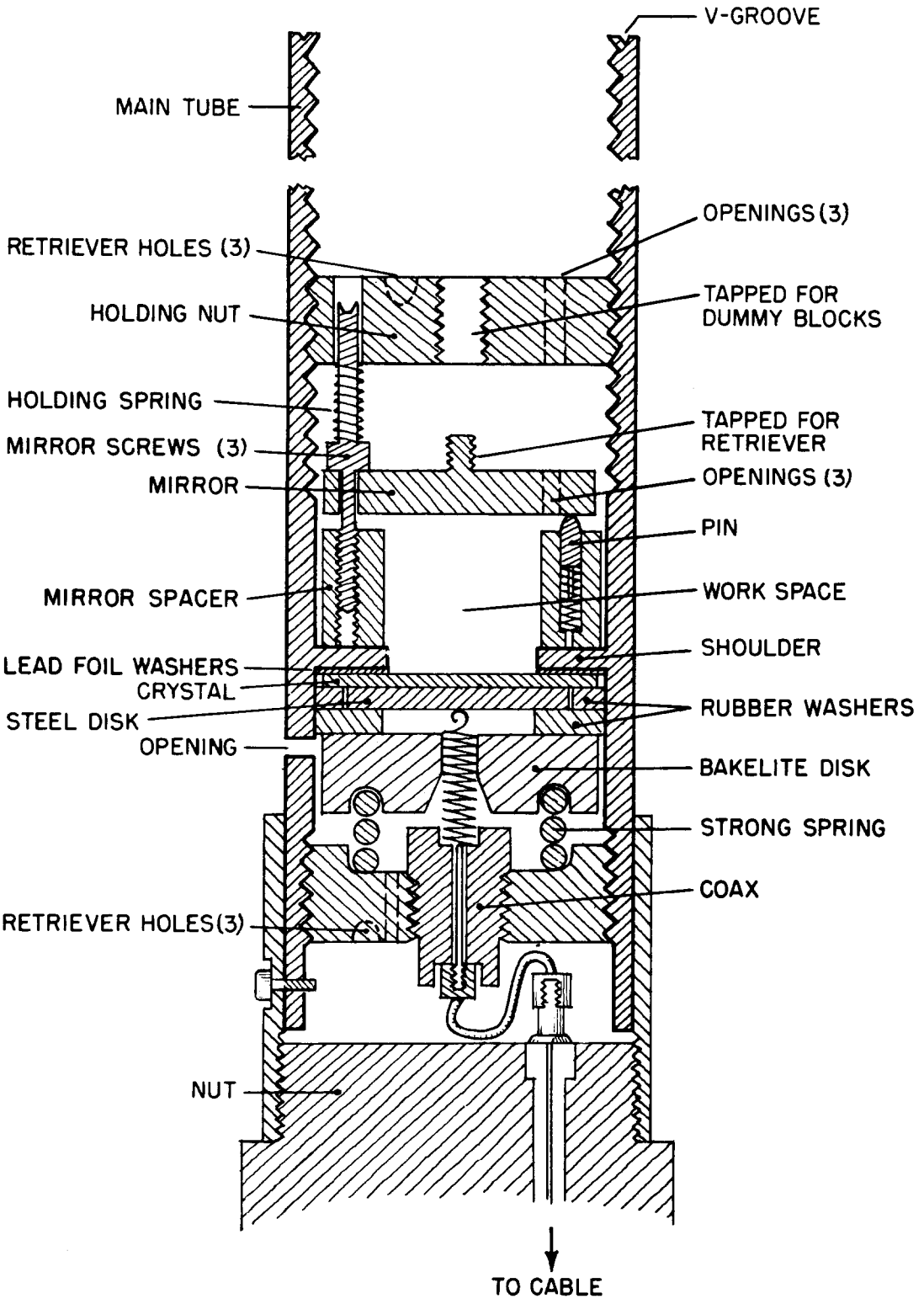


PLATE 2



CARTRIDGE AND MIRROR ASSEMBLY

FIG. 2

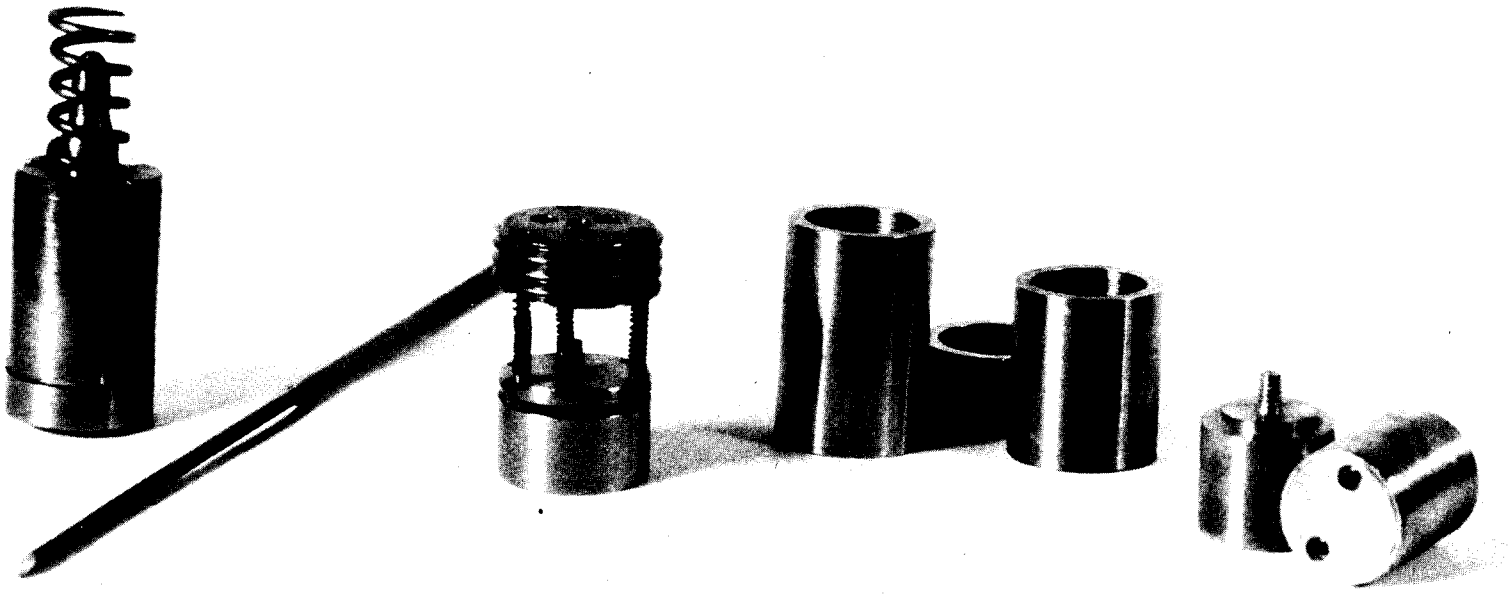
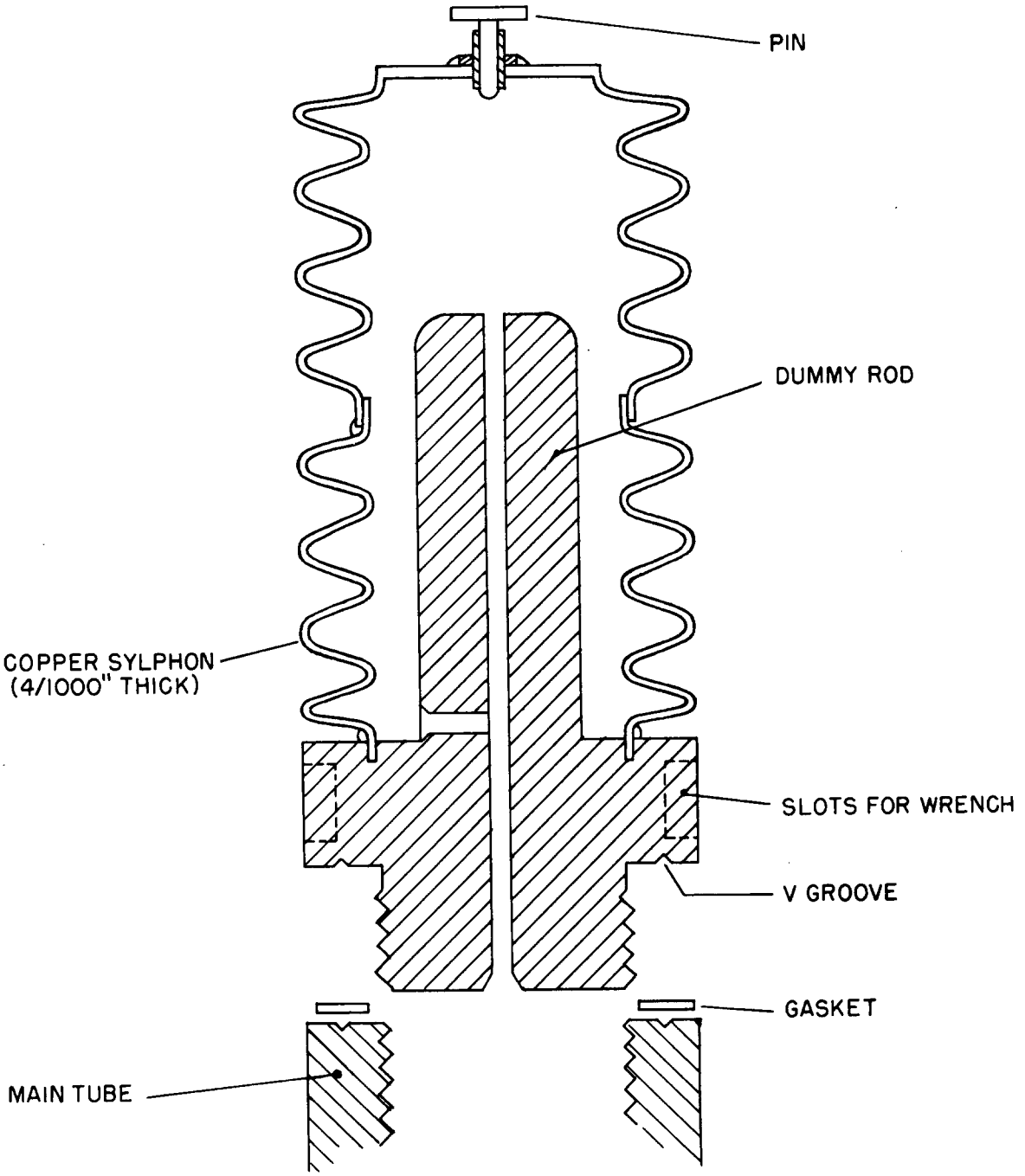


PLATE 3



SYLPHON ASSEMBLY

FIG. 3

the greatest problems of design and construction, and is still, perhaps, less satisfactory than the rest of the equipment. Figures 2 and 3 and Plates 2 and 3 refer to the component parts of the cartridge models. All data discussed in this paper were taken with the cartridge to be described, except that in a few cases the supporting steel disk behind the crystal transducer was omitted - a detail of no particular consequence for the data.

The most severe design consideration, apart from the demands of the theory of sound propagation and the velocities and absorptions expected, was the inner dimensions (0.8 inch i.d.) of the 12,000 kg/cm^2 pressure cylinder in which we hoped to place the cartridge. This cylinder never became available, however, and a somewhat larger one (with a 1-inch internal diameter) had to be used throughout the runs, though its weak construction prohibited its use much beyond 6000 kg/cm^2. This explains why the design of the cartridge is somewhat more closely spaced than necessary in the runs here reported, and why the pressure range was limited to 6000 atmospheres.

The whole structure is mounted on a sleeve screwed onto the nut that plugs off the pressure cylinder at the end (Fig. 2 and Plate 2). A coaxial cable, insulated from the nut itself by pressure-supporting mica disks, carries the power from a standard coaxial connector on the outside to a threaded stub inside the pressure cylinder. In Fig. 2 the further course of the power pulse can be followed up through a copper-in-bakelite coaxial section, along a spring (of far fewer turns than drawn here), and through a steel disk to the gold-plated lower side of the transducer. The front, or upper, face of the crystal, also gold-plated, makes contact with the main stainless steel tube through three lead washers (each 0.002-inch thick) and thence to ground through the metal sleeve, nut, and pressure cylinder. The scale of the drawing may be judged by the diam-

eter of the crystal disk - i.e., 5/8 inch .* Under pressure the various components will shrink in varying degrees. For this reason no cement could be relied on to hold the crystal into place, and placement was secured by spring-clamped edge support. Furthermore, soft rubber washers distribute the spring's force of several kilograms in such a way as to prevent interchange of the liquids on the two sides of the crystal - that is, the liquid under observation on the front side, and on the other side the pressure-supporting petroleum ether which fills the pressure vessel, surrounds the cartridge tube, and enters through the indicated opening into the lower part of the cartridge.

It will be noted that the whole lower part can be disassembled to allow replacement of the crystal. As experience accumulated, it was finally possible to take one assembly unchanged through ten or more pressure runs. A wholly "permanent" cartridge would be most desirable, if only because, ideally, absolute attenuation determinations by our method require at least two successive runs with unchanged crystal assemblies. Actually, a really permanent cartridge cannot be hoped for because the front face of the crystal deteriorates over a period of time by loss of plating and pitting of the quartz surface in use. Moreover, the rubber washers eventually freeze and crack, requiring periodic replacement.

Without the stainless steel disk to back up the crystal, the cost of replacement because of breakage during assembly or pressure changes, would have been prohibitive. No doubt the presence of the disk distorted somewhat the pulse shape of the echoes by internal reflections, the reflection time in the steel disk being about 0.5 μsec. Nevertheless, by visual com-

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*The thickness of the crystal in Fig. 2 is of course exaggerated. The gold plating on its lower or back face is recessed 1/16 inch from the edge to prevent sparking-over.

parison of the echo pattern, the coupling between quartz and steel was thought to be sufficiently small to justify the use of the backing disk despite its possible drawbacks.

The type of crystal-clamping employed in these experiments seemed necessary for an assembly which must be useful for work on all kinds of liquids, including conductors and solvents. Here, too, the decision entailed other less desirable consequences. For example, clamping voids the assumptions which underlie the theoretically purely longitudinal vibrations of the X-cut crystal. The distortion of the wavefronts sent out may therefore be serious,[115] particularly if the disk is not cut according to a Straubelumrandung.[5,131,138] Useful suggestions on insulation and clamping of the crystal will be found in References 17, 47, 56, 115, 130, and 135.

If any of these devices should be adopted, it would also seem a primary necessity to provide a method of selecting for treatment only those crystals which, even in the unclamped stage, actually do send out a reasonably plane-wave system. That there is legitimate doubt on this point was shown by J. Quinn,[115] who found by a check of the acoustic field in front of the crystal that only one commercial crystal in fifteen approaches the theoretical case of a piston-vibrator. There was much evidence in the present research of the validity of his assertion.

Tests of leakage of the assembly described were made in two ways. In one test, the liquid contained in the work space above the crystal was distilled water while the pressure-communicating liquid in the cylinder and in the lower part of the cartridge was salty water. After application and release of pressure, the conductivity of the water in the work space was tested and found substantially unchanged. In the second test, conducting water was put into the work space and the pressure-communicating liquid outside was petroleum ether. The d-c resistance across the crystal was tested throughout the

pressure run, but remained higher than 0.1 megohm. The work space above the crystal is sealed off liquid-tight by means of a sylphon assembly (Fig. 3) which screws into the top of the main tube. Leakage past the joint is effectively prevented by lapping the touching shoulders, except for a circular V-groove in each, which is fully packed by a rubber gasket when the sylphon is tightened against the main tube.

Before assembly, the sylphon, which is made of flexible copper sheets 0.004 inch thick, is filled with the same liquid as the work space itself. The dummy rod indicated in Fig. 3 serves to increase the fractional compression which the total amount of liquid in the upper cartridge can undergo without danger of crushing the sylphon or the crystal. Additional sylphon sections may of course be added if greater compression is expected.

The flexibility of the sylphon assures that the liquid in the work space is at the pressure of the surrounding pressure-conducting medium. It also permits changes in temperature between pressure runs on an unchanged assembly. Plate 2 shows the complete arrangement, with a four-section sylphon in place, as it looks just before insertion into the lower pressure cylinder. Actually, the position of the optically flat steel mirror in the work space is adjusted for parallel alignment with the crystal just before the sylphon termination is put in place.

There is no way to compensate for minute changes in the position of the mirror once a run has begun. Such changes (i.e., tilting and warping) of the mirror face with respect to crystal eventually do take place in most pressure runs, for reasons that range from tiny dust particles under the supports to relief of residual strains in the metal. As will be seen, the tilting of the mirror by a few seconds of arc is sufficient to make the measurements of attenuation quite difficult; how-

ever, the measurements of velocity are not seriously affected.

Many modifications of the mirror system have been tried, and others are being planned; the one shown in Fig. 2 was the final design, found most satisfactory up to this point in respect to both reduction of tilting and convenience of initial adjustment. This adjustment is obtained by watching the echo-pattern while turning the three screws that hold the mirror aginst the thrust of the three recessed pins in the mirror-spacer. A high-order echo will respond very sensitively, in amplitude and pulse shape, to the slightest adjustment once alignment between mirror and crystal has been achieved. The problem of mirror alignment has always been a difficult one in such research.[1,81 82] The pressure changes, which are sometimes uncontrollably sudden, only aggravate this trouble, which is similar in some respects to the irregularities obtained with piezometers that have undergone a shock.*

Plate 3 shows a mirror system which has now been discarded. To the left is shown a screw-driver for the mirror screws; next, the mirror assembly described above; and a set of three lapped stainless steel spacers, chromium-plated like the rest of the mirror system and main tube, for additional rust protection. The steel spacers whose lengths were known to within 0.0001 inch could be added below the mirror spacer to increase the sonic path. Lastly are seen two of the dummy blocks which could be screwed into the holding nut above the mirror to fill "dead" space and so to increase the effective maximum compression of the liquid in a given assembly.

Receiver

Following the path of an echo out of the cartridge and pressure cylinder the receiver is reached over a short section of 75-ohm coaxial cable. The 15 Mc/s receiver which is based

*Physics of High Pressures, p. 122

on the commercial W-6-C amplifier design was built to provide about 100-db amplification with a bandwidth of over 2 Mc/s, followed by two stages of video amplification. In actual use the range of amplification obtainable was less than 80 db before either self-oscillation began or the signal-to-noise ratio became too low. This proved no handicap during these runs, however. Noise was reduced by filtering the power supply. The calibrated gain control, read by means of a chart in decibel gain, is indicated in Fig. 1; the balance control, which applies a selected variable square blanking pulse from the Loran set every 0.02 second , is not shown. The "gain control reading" (G.C.) mentioned in subsequent tabulations of data is the indicated number of divisions on a dial mounted on the gain control potentiometer that determines the plate voltage in three of the amplification stages of the receiver. For calibration purposes the level of the received signal was set by controlling the plate voltage on the pulser. A known amount of attenuation was then inserted by means of a calibrated attenuation box between the crystal and the receiver. This attenuator is a switch-operated constant input-impedance strip based on the so-called Beer's design[53] and probably was accurate to better than 0.1 db.

A small standard broadcast receiver with accurately calibrated dial was used for frequency-monitoring of the power supplied to the crystal. Its sensitivity was better than $\pm$0.05 Mc/s for our pulses.

Pressure Equipment

The remaining accessories indicated in Fig. 1 and Plate 1 include the pressure plant and the thermostated bath. The main pump and priming pump were both hand-operated; machine-operated models, had they been available, would probably have given better results with less inconvenience. The details and apparatus of the high-pressure method of Professor Bridgman are too well known to require description here.

Pressure measurements were made by way of measuring with a Cary-Foster Bridge the resistance of a standard manganin wire coil placed in the upper pressure cylinder. The calibration of the coil by two checks of the freezing pressure of mercury at 0°C yielded the value of 4.58-cm change in the resistance bridge setting for a change or 1000 kg/cm^2 in the pressure. The gauge is sufficiently linear over the range of pressure and temperature here discussed. Since bridge settings were ascertained to 0.1 mm, the accuracy of the pressure data should be 2 kg/cm^2. The maximum error over the whole range in the absolute pressure data expected, because of irregularities in the wire, is at most 10 kg/cm^2. This possible discrepancy may be ignored until discovery is made either of large values of $\partial u/\partial p$, or of definite discontinuities and critical points on the velocity or attenuation curves.

Temperature Control

An asbestos-lined metal drum filled with range oil served as the temperature bath into which the lower pressure cylinder cartridge was immersed. A thermostated heater, based on Benedict's design,[11] provided regulated power to 500 watts, keeping the temperature of the bath to within ±0.02°C at the thermo-element once the control had "settled," with only occasional slight manual adjustment. At control temperatures much above room temperature, however, the performance was not always quite so satisfactory. Actual temperature readings, recorded to 0.01°C, were taken with a calibrated mercury-in-glass thermometer the bulb of which was pressed against the submerged pressure vessel. The bath itself was thoroughly and continuously agitated by a motor-driven stirrer, yet temperature inhomogeneities in the range oil of the order of 0.05°C were noted. Undoubtedly, the large amount of metal in the cylinder surrounding the cartridge smooths out such local temperature differences.

The magnitude of the thermal lag in the pressure cylinder is surprisingly high. A sudden change of a few degrees in the temperature of the bath did not begin to penetrate and to affect the sensitive echo pattern for almost ten minutes. Accordingly, precautions were taken to attain thermal equilibrium before recording any data.

IV

Procedure

The steps followed in the preparation of equipment and the taking of measurements are to some extent expressed or implied in the foregoing. Routines were developed to prevent any possible contamination of the liquid under test. The liquids investigated were taken from fresh bottles of the purest grade available in the laboratory, except for the sample of ether which appeared to have been opened once before. The water in particular was from a sample purer than necessary, multiply distilled and contained in pyrex.

After the mirror assembly had been adjusted, the cartridge inserted, and temperature equilibrium attained, the "zero" reading (at zero additional pressure) was made on the bridge. It developed that the electronic equipment had to be allowed to run for about an hour before repeatable measurements could be undertaken.

Next, one or more preliminary runs were made up to about 2000 kg/cm^2 (the priming pressure), to check any gross deficiencies in the stability of the mirror alignment. Repeatability of the zero reading at the end of the run gives a measure of confidence in the alignment, but "reversible" anomalies (in warping and tilting due to pressure changes) are not inconceivable; nor is anything guaranteed for future runs, particularly if they are carried beyond the priming pressure range. A seasoning run over the whole pressure range involves disassembly and repacking of the piston arrangement between runs, and when tried out during one experiment did not appear to be more satisfactory than the shorter seasoning run. Thus, seasoning runs can help significantly in only two ways: by uncovering irreversible misalignment difficulties, and by pre-

paring a newly assembled crystal system by initial accommodation of strains introduced during assembly.

As will be shown, there are many causes for the possible distortion of the pulse shape of higher-order echoes which would preclude their use in the measurement of either velocity or attenuation, or both. It is, however, easy to pick out "good" echoes from the whole pattern. The following representative table indicates how satisfactory the method is for consistent velocity measurements. The substance used was water at 25°C, before additional pressures were applied. The readings of time, Δt in μsec, refer to the interval between the first pulse and the indicated echo as measured on the Loran screen.

Table I

Number of echo	Δt(μsec)	Time per echo (μsec)
38	451.5	11.88
36	427.0	11.86
32	380.5	11.89
28	332.5	11.88
16	190.0	11.88
6	71.5	11.9
2	24.0	12.0

The accuracy of each reading of Δt being about ± 0.5 μsec, it is evident that the higher-order echoes are the ones of interest for precision measurements; among these, the agreement of better than 2 in 1000 is indicative of the possibilities (and limitations) of the multiple-echo method using the Loran presentation unit.

In the tabulation above, all randomly selected "good" echoes were listed. An example of the errors made by using echoes with obviously poor pulse shape is indicated in the result for the 23rd echo, whose Δt was uncertain between the

limits of 279.5 and 272.5 μsec. The time per echo for these extremes is 12.15 and 11.85 μsec. There is no reason why the results of such obviously distorted pulses should be included in the calculations, as Huntington has done in recent work on solids.[82] All results in this paper refer to sets of undistorted echoes.

The procedure for attenuation measurements has been discussed. The ideal exponential decrease of echo-amplitudes cannot strictly be expected in a system where losses occur at the mirror and crystal surfaces, and where the position anomalies discussed above contribute to irregularities in the amplitude ratio between successive echoes. This is shown in a representative set of measurements in water at 24.5°C for the first 17 echoes (Table II).

The uncertainty in individual measurements is about ±0.25 db if two well-shaped pulses are compared, but may surpass ± 2 db with poor pulses. This rules the latter out of measurements on attenuation.

The values of attenuation per echo in the table below is 4 db/echo for the first half of the set, and 4.3 db/echo for the whole set. This difference indicates the error limits to be expected. A consistency of ±10 per cent is considered good in almost all papers on attenuation measurements. Estimates of 30 per cent or more are recorded in some methods used in recent literature.[49,82,113,145,152] It is believed that the echo method is inherently capable of greater accuracy than any other, and further modifications of the cartridge assembly are planned to reach that goal.

For the present it is sufficient to focus our attention on a few echoes throughout each run and so to obtain both velocity and attenuation measurements simultaneously. If some of these echoes get progressively worse as the pressure is changed, operation may be continued with the remainder. If the whole pattern becomes disturbed, it may be necessary to forego further attenu-

Table II

Number of echo	db attenuation	Difference between successive values (db)
1	0(level)	- - -
2	3.5	3.5
3	8.5	5
4	14	5.5
5	18	4
6	21.5	3.5
7	24	2.5
8	28	4
9	32	4
10	36	4
11	40	4
12	45	5
13	48	3
14	54.5	6.5
15	58.5	4
16	65	6.5
17	68.5	3.5

ation measurements for the time being, though useful velocity measurements can generally be taken throughout every run. It is evident that reliable judgment for these situations is a matter of accumulated experience.

As the pressure is slowly increased, the presentation unit is watched for any sudden changes. In the absence of points of obvious interest, readings are taken at approximately 500 or 1000 kg/cm^2 intervals. Before the data are recorded, several minutes are spent waiting for the heat of compression to dissipate. Some readings are taken during the subsequent decrease of pressure, and at the end of the experiment the cartridge is opened to check on the purity of the liquid under test. The time involved, from one assembly of the crystal system to the next following one, gradually decreased from about 16 to 8 hours as better routine methods for the various operations were found.

V

Velocity Measurements - Errors

Since the number of errors theoretically expected in our tests was large, it seemed logical to try a preliminary experimental determination of some well-known velocity of sound in a liquid, under conditions corresponding to actual pressure runs, and with precautions based on an analysis of expected errors. A prototype of the cartridge system discussed above was filled with pure water at atmospheric pressure and 26.20°C. A removable spacer of 0.5000-cm length was introduced below the mirror assembly, and the delay of a convenient high-order echo was noted with respect to the first echo. Then the spacer was removed, and the measurement repeated. In the first case, the difference between the first and 26th echo was 545.5 μsec, measured on the Loran screen, or 21.82 μsec/echo; in the second, using the 39th echo, the difference was 576.0 μsec, or 15.15_8 μsec/echo. Since the difference in sonic paths was 1 cm, the velocity of sound at 14.8 Mc/s in the liquid comes to $1.501_1 \times 10^5$ cm/sec by our experiment. The standard velocity at that temperature, using the results of Schreuer[131] and Seifen,[132] usually cited as the best, is 1.5002×10^5 cm/sec. The difference of 0.06 per cent between experimental and standard values is somewhat less than the error inherent in the readings themselves.* We see that unless the errors were likely to increase unexpectedly in other liquids or at other pressures, there was no reason to be particularly concerned about

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*This was an example of a velocity determination by the spacer method. Attenuations may be found similarly if extreme care is taken that the mirror does not tilt or warp in the slightest during the change of spacers. This may be possible at atmospheric pressure, but is too difficult at present to apply under conditions of changing pressure .

them.

In the extensive bibliographies of References (34) and (123) are listed many attempts to fix the source and magnitude of possible errors in velocity measurements. The estimated accuracy of experimental velocity values ranges from 1 per cent in Bancroft's work[3] to about 0.01 per cent in Schreuer's,[131] but the difference between the experimental data and the theoretical value obtained from the wave equation may be larger under some conditions. These will be discussed presently.

Speeding Up of Echoes

The data in Table III were gathered by using an A/R 'scope instead of the Loran set to read off accurate time intervals between echoes. Water at 24.10°C and atmospheric pressure is the liquid under test. The readings, to ±1 unit, refer to the settings of the heliopotentiometer on the A/R 'scope, on which 200 units correspond to a delay of 12.192 μsec between a fixed reference signal and the received echo.* The gain control settings are given to illustrate the relative level of signal. Between 10 and 30, the gain of the receiver increases by about 24 db.

The values of $(\Delta + \varepsilon)$, which are proportional to the time of travel per echo, show strikingly that the velocity of the first few echoes is apparently greater than that of subsequent ones in the ratio of about 37.5 μsec to about 37.1 μsec.

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*The correction ε has to be added to the straight reading of units of delay indicated on the heliopotentiometer of the A/R 'scope to compensate for small unevennesses on the internal potentiometer wire that controls the delay of the sweep. This calibration was made by means of the superposed crystal-controlled marker pattern which has a periodicity of 200.0 delay units for 12.192 μsec at the particular sweep speed selected for this work. This calibration may be unnecessarily refined for the present, but for velocity measurements on solids the exact error curve will be of greater importance if the A/R 'scope should again be used for precision checks.

Table III

Number of echo	Reading	Difference Δ*	ε	Δ + ε	Setting of gain control
1	569	605	5	610	(approximate)
2	1174	609	2	611	
3	1783	610	2	612_5	10
4	2393	610	2^5	612	
5	3003	609	2	611	
6	3612	610	1	611_5	20
7	4222	612	1^5	613_5	
8	4834	613	1^5	614	
9	5447	611	3	614_5	30
10	6058	612	2^5	614_5	
11	6670	614	0^5	614	
12	7284	614	0	614	
13	7898	614	0	614	
14	8514				

*Difference Δ represents the difference between the reading on the same line and that on the following line in the table.

In explanation of this disturbing result, which might well blight all research on sound velocity that relies on the first echo only,[113] a simple and attractive idea might suggest itself; that this speeding-up of the earlier echoes is a temperature effect. Schreuer had noticed the same effect in his precision work on water. One would have to postulate that the power pulse releases enough heat near the crystal to speed up the earlier sound pulses, but that this heat is dissipated within about 100 μsec so that later echoes are unaffected. Calorimetric calculations make this hypothesis unlikely for the low powers here employed. The conclusive argument against the explanation in terms of temperature effects is that the same phenomenon can be observed in water at about 6000 kg/cm^2 pressure where the temperature coefficient of velocity is no longer

positive but turns negative. Tables IV and V show conclusively that the speeding-up of earlier echoes is observed in ethyl alcohol and nitrobenzene, both of which have large negative values of $\partial u/\partial T$ (more than -3×10^{2} cm/sec/°C). In fact the slight speeding-up of the first few echoes was noticed in every substance tested.

A more consistent explanation for the speed-up of the first echoes depends on the fact that the pressure coefficient of sound velocity is always positive and of the order of 5×10^{-4} cm^2/kg; so that at greater amplitudes, where the sound pressure has been reported to reach several atmospheres, the velocity change should be to higher values. This is equivalent to suspecting a breakdown at the higher signal levels of the usual assumptions in the statement of the wave equation. Following Wood's treatment,[149] the velocity (u) of a wave with finite amplitude is related to velocity (u_o) of a wave with infinitely small amplitude by

$$u = u_o\left(1 + \frac{\partial \rho}{\rho}\right)^{\frac{\gamma + 1}{2}}$$

ρ is the density, γ the ratio of specific heats of the medium.

The actual numerical check is not satisfactory. Even assuming an initial sound intensity I of about 15 watts/cm^2,[33] the sound pressure amplitude P, which is given by

$$P = \sqrt{2\rho u I}$$

is only about 7 atmospheres; and using, as an example, water at 1 atmosphere and 30°C, where $\rho^{-1}\frac{\partial \rho}{\partial p} = 4 \times 10^{-5} cm^2/kg$, the expected velocity change comes to three parts in 10,000. This change is in the direction observed, but about one order of magnitude below the observed speed-up.

The measuring method itself comes under suspicion next. A likely explanation for the observations of shorter time intervals between the earlier echoes would presuppose two conditions:

Table IV

Ethyl Alcohol

Number of echo	Reading	Δ	ε	Δ + ε	Gain Control
1	708±1				
2	1464	756	6	762	
3	2225	761	1	762	
4	2988	763	3.5	766.5	above 10
5	3751	763	2.5	765.5	
6	4513	762	2	764	
7	5278	765	0.5	765.5	
8	6040	762	2.5	764.5	
9	6804	764	3	767	
10	7570	766	0	766	

Table V

Nitrobenzene

Number of echo	Reading	Δ	ε	Δ + ε	Gain Control	db*
1	871				7.5	--
2	1784	913	5	918	8.5	--
3	2699	915	3	918	17.8	10
4	3615	916	3.5	919.5	29.5	23
5	4532	917	2.5	919.5	49	35
6	5451	919	1.5	920.5	72	48
7	6364	913	7	920	102	62

*Zero db reference level = gain control setting of 10.0

(1) By virtue of temperature inhomogeneities in the test liquid, selective attenuation of high-frequency components, etc., the pulses become somewhat broader as they traverse the crystal-to-mirror distance the first few times; (2) in the timing of echoes, undue but perhaps unavoidable emphasis is placed on the front part of the echo pulse rather than on the peak of the complete pulse shape.

The truth probably lies in some combination of the effects of intensity and of method of measurement. It was found that substantially no speed-up occurred when the intensity of the echoes had dropped to a point where the gain control had to be increased to 10 or higher to observe the echo on the screen. This was true even for the first few echoes if the initial power pulse had been attenuated below the critical value by a suitable decrease of plate voltage on the 829 tube in the crystal driver circuit. Corresponding precautions were taken on velocity measurements.

These conclusions should be of particular importance in any work where only one or, at most, a very few echoes can be used, as, for instance, in highly absorbing materials. It should be noted that as long as the time-per-echo is obtained by averaging the time over a large number of echoes, the error due to initial speed-up is quite negligible.

Pulse Distortion

Closely allied with the foregoing paragraphs is a discussion of errors in velocity measurements owing to pulse-shape distortion. The several sources of distortion which had to be considered in the design and operation of the equipment included the following:

1. Phase distortion in the receiver circuits.
2. Selective attenuation by the medium; since the attenuation constant α is proportional to the square of the fre-

quency, the higher frequency components of a very short and rectangular pulse would soon be lost in transit. The pulse length in these experiments was therefore chosen in such a way that the ratio of the frequency-independent attenuation factor, α/f^2, of the extreme components in the spectrum was less than 1.2.

3. Temperature gradients across the wavefront; they were minimized by keeping the repetition rate and the applied power low, and by waiting for the best reasonably obtainable temperature equilibrium before readings were taken.

4. Deviation of the vibrations of the X-cut crystal from the theoretical pure piston motion.

5. Deviation of the crystal and mirror surfaces from ideal plane parallelism.

6. Ringing of crystal after cessation of the applied pulse.

7. Mixing at the crystal of echoes with stray reflections, either from the walls or from the steel disk in back.

8. Normal beam-spreading and other diffraction effects which cause large phase differences across the wavefront, particularly during the first half-meter of travel of the pulses.

Some of these points have been discussed earlier; others will be examined later in connection with the error sources in attenuation measurements. Perhaps the worst of these is the source pointed out in (8), particularly if others (e.g. (3) and (4)) are simultaneously active. The wavelength of sound under these test conditions is of the order of only 0.01 cm; consequently the wavefront is easily disturbed.

Effect of Tube-Walls on Velocity

The effects of viscous drag and thermal conduction to the walls are well known.[102,149]

In this research the tube radius was about 0.5 cm; the

values of the viscosity, μ, and the thermal conductivity for the tested liquids over the whole range covered, remained so low that the correction factor for velocity due to these sources was less than 1 part in 10,000. At higher pressures, however, and with more viscous liquid, particularly near the freezing point, one may expect an observable effect.

Effect of Attenuation on Velocity

The term u_o in the wave equation

$$\ddot{\rho} - u_o^2 \nabla^2 \rho - \rho^{-1} \left(\frac{4\mu}{3} + \mathcal{K}\right) \nabla^2 \dot{\rho} = 0$$

refers to the velocity in the absence of any viscosity. (The other terms are further defined on p. 47). Actually, however, attenuation is present, and the observed velocity should accordingly differ from the theoretical one. The discussion in Reference (123) and standard texts reveals that the difference between these two velocities is less than 1 part in 10,000, but might become noticeable at higher attenuations.

Change of Sonic Path with Pressure

This is an appreciable but easily calculated effect. $\Delta\ell/\Delta p$, for the steel spacer used here, reaches a few tenths per cent at 6000 atmospheres; the exact values are included in the calculations of velocity in the next section.

Summary

Errors in velocity measurements can come from numerous sources, but in the present research they have either been prevented by a proper choice of experimental conditions, or have been allowed for by exact calculations, or are by nature below the limits inherent in individual readings - which are at present about 2 parts in 1000 using the Loran set, and 1 in 1000 using the A/R 'scope.

VI

Velocity Measurements - Results

Experimental Results for Water

Velocity measurements of sound in liquids at various temperatures and pressures are of interest for several reasons: the value of several thermodynamic coefficients may be determined or checked with respect to static measurements; pressure coefficients of sound velocity, and temperature coefficients at given pressures, may be found directly; regions of dispersion may be investigated, even if only a single frequency is impressed on the sound source, etc.

Experimental results of the velocity of sound in distilled and gas-free water are given in Figs. 4, 5 and 6. These examples are intended to indicate the applicability and limitations of the multiple-echo method for this kind of investigation.

Figure 4 represents the typical result for a run on which the Loran receiver was used.

A considerable number of experiments were made at this temperature (30.00°C ±0.05) using different cartridge models, spacer and mirror designs, sylphon assemblies, etc. In fact, this type of run was chosen as the standard for experimentation on the equipment itself. Nevertheless - and this fact amply bore out our initial expectations of the method - none of the corresponding experimental data obtained during any of the various runs deviated by more than 4 pro mille at any point from the curve shown in Fig. 4; the average deviation was about the same as the uncertainty of 2 pro mille inherent in each individual measurement of this run.

The curves in Fig. 5 refer to data taken at temperatures

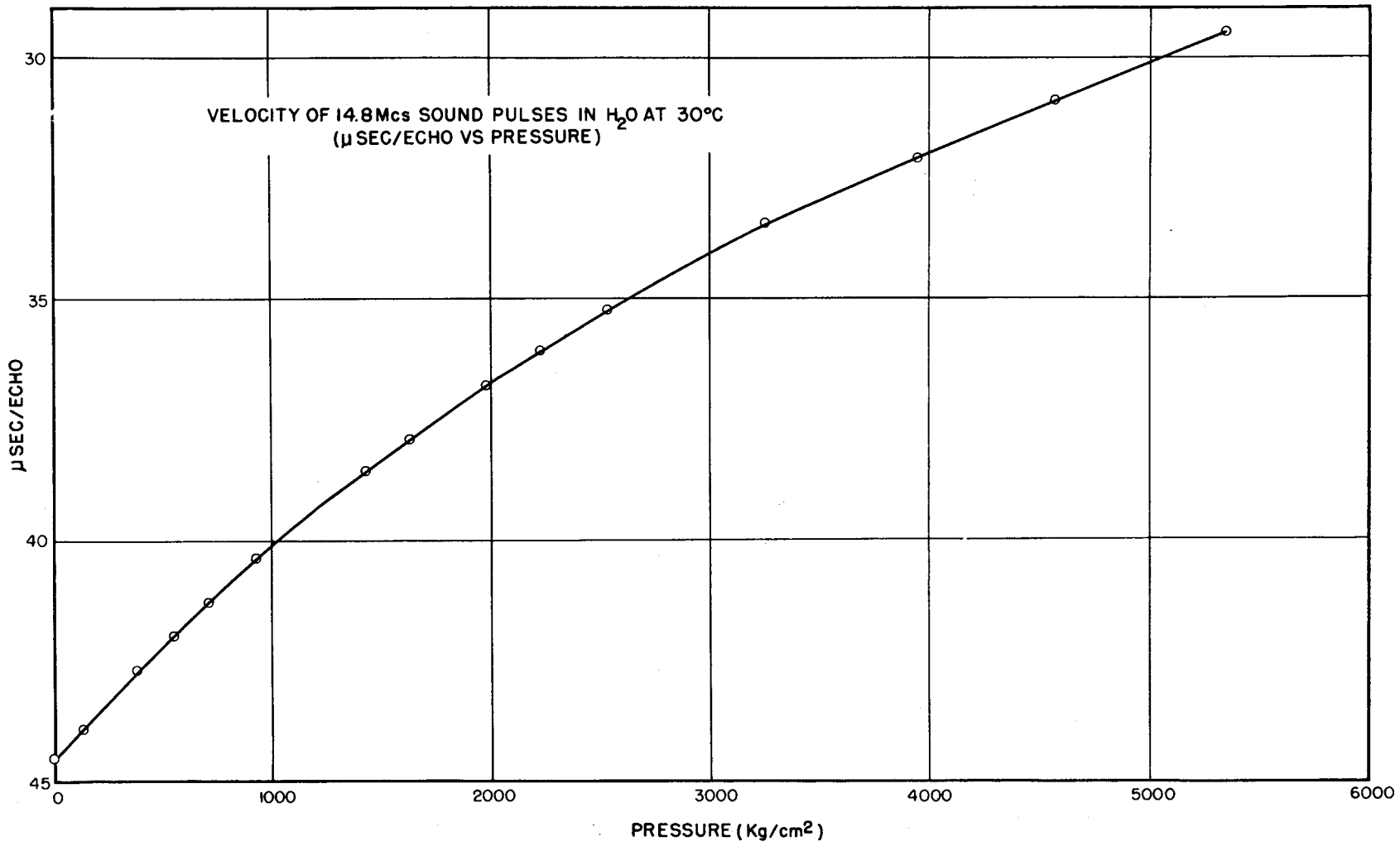
VELOCITY OF 14.8Mcs SOUND PULSES IN H_2O AT 30°C
(μSEC/ECHO VS PRESSURE)
μSEC/ECHO
30
35
40
45
0
1000
2000
3000
4000
5000
6000
PRESSURE (Kg/cm²)

FIG. 4

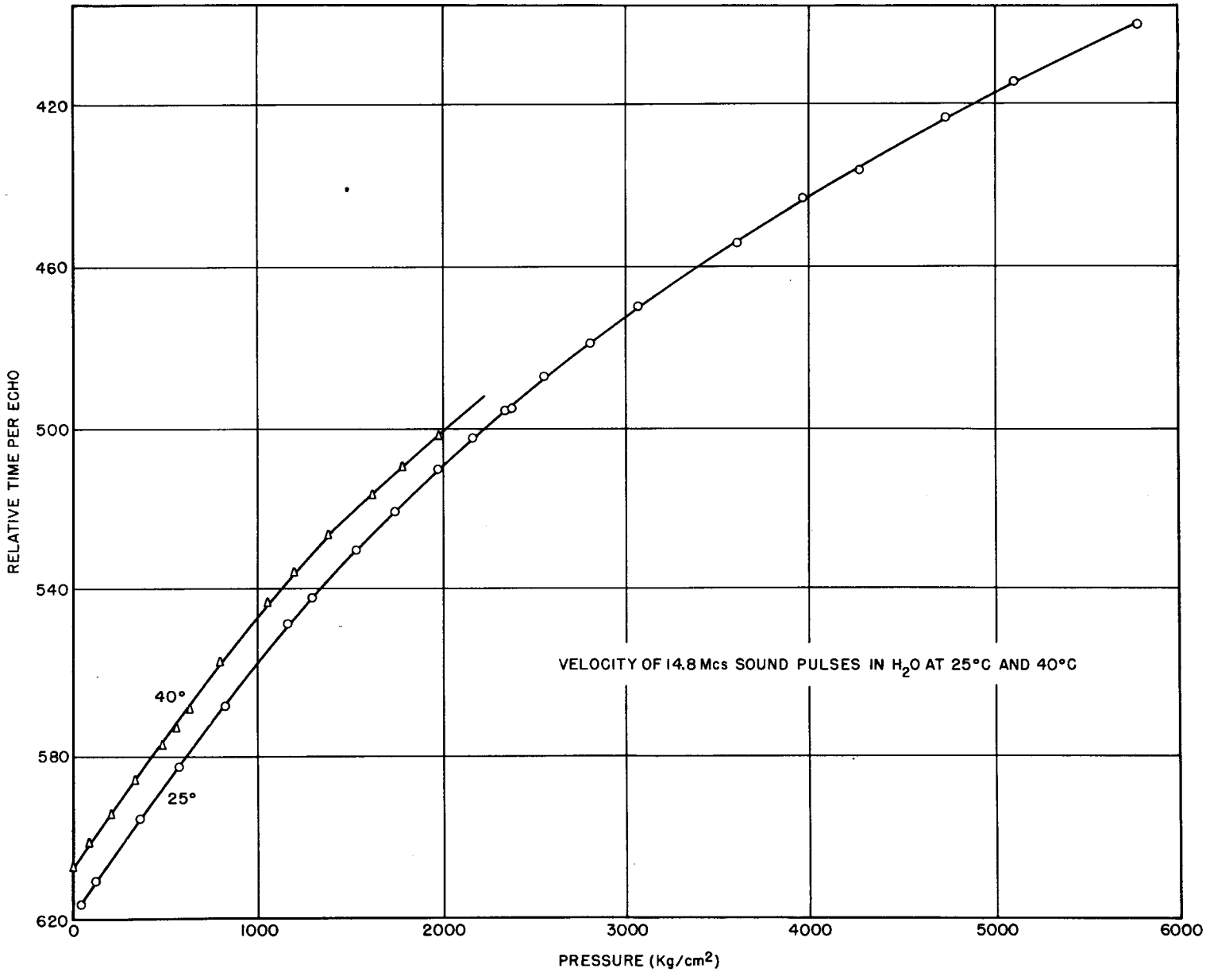
420
460
500
540
580
620
0
1000
2000
3000
4000
5000
6000
RELATIVE TIME PER ECHO
PRESSURE (Kg/cm2)
40°
25°
VELOCITY OF 14.8 Mcs SOUND PULSES IN H2O AT 25°C AND 40°C

FIG. 5

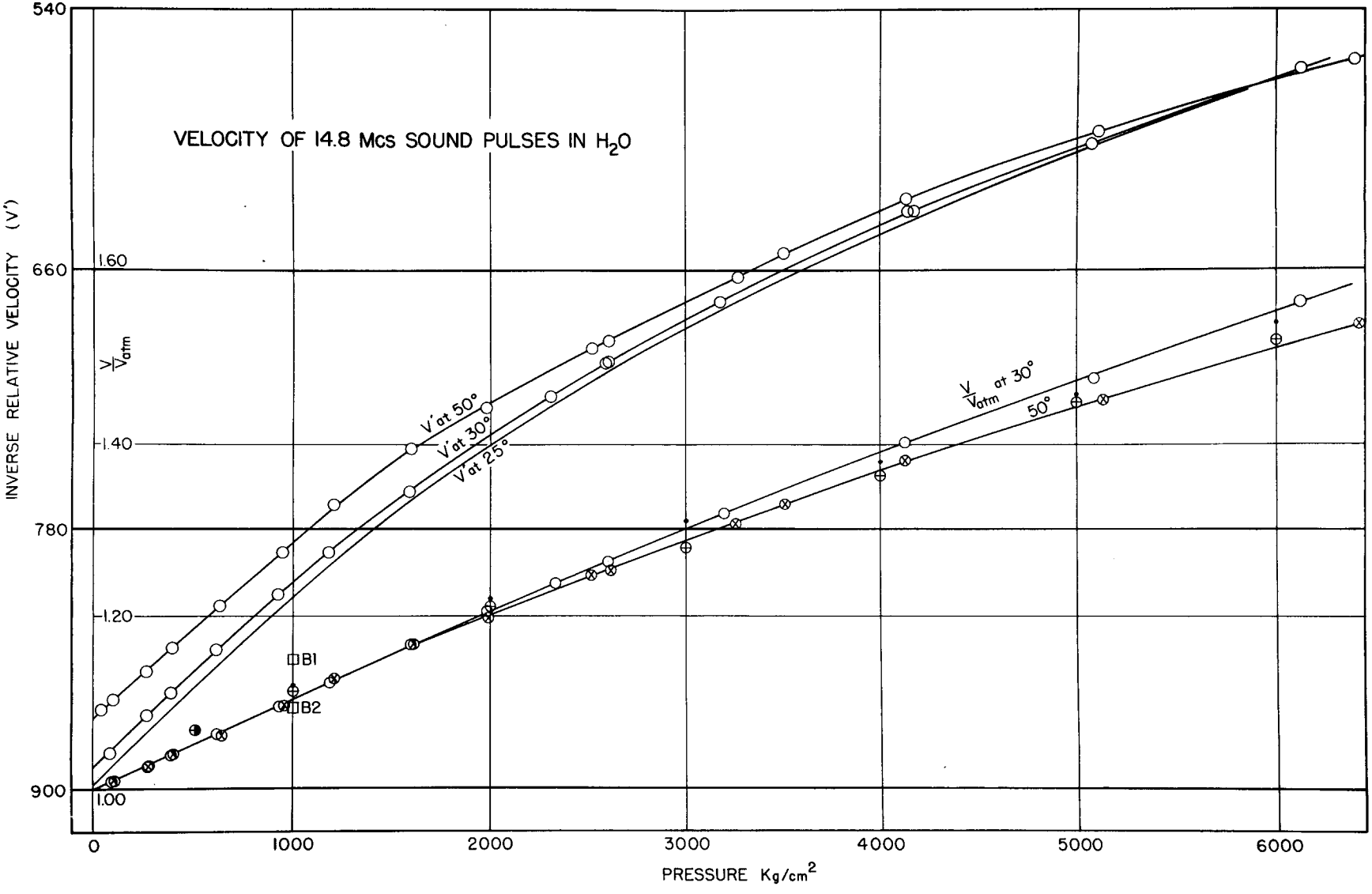
VELOCITY OF 14.8 Mcs SOUND PULSES IN H_2O
INVERSE RELATIVE VELOCITY (V')
540
660
780
900
1.60
1.40
1.20
1.00
$\frac{V}{V_{atm}}$
V' at 50°
V' at 30°
V' at 25°
$\frac{V}{V_{atm}}$ at 30°
50°
B1
B2
0
1000
2000
3000
4000
5000
6000
PRESSURE Kg/cm^2

FIG. 6

of 25°C and 40°C. These data are plotted for relative time per echo instead of microseconds per echo, and so correspond more closely to actual experimental information obtainable with an A/R 'scope. The latter was used for several runs to check the accuracy of velocity data obtained by the Loran method. "Relative time" or "relative inverse velocity" refers therefore to the number of units found with the heliopotentiometer of the A/R 'scope that corresponds to the delay between successive echoes.* The accuracy of velocity data so obtained is about 1 in 1000.

The two curves are intended also to show, side by side, a poor and a good run on water. It will be noted that the data at 40°C are more than usually scattered at low pressures; the crystal finally broke (as it frequently did during the earlier measurements) while taking the pressure through the by-pass point at 2000 kg/cm^2. It would appear that the crystal was under some initial strain, perhaps as a result of uneven clamping at the edges, and, too, that the transition was made too quickly.

The most important data on the velocity of sound are summarized in Fig. 6. To facilitate comparison, two sets of curves have been entered above the identical abscissa. The upper set of three curves refers to the ordinate at the extreme left and serves to compare the absolute velocities of sound at 25°C, 30°C and 50°C. The experiments at 50°C and 30°C were among the last made and are probably the most satisfactory and reliable. For example, the repeat points observed during the decrease of pressure, check most gratifyingly. "Inverse relative velocity" again refers to average delay per echo.

The lower set of two curves plots the more useful quantity, velocity (u) at given pressures divided by velocity (u_{atm}) at

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*200 units corresponds to 12.192 μsec delay. The correction factor ε is included in each of the readings plotted.

the atmospheric pressure and the same temperature. The higher line of the two (empty circles) is for 30°C, the lower (x in circles) for 50°C. In either case the deviation of any one experimental point from a smooth curve is at most 3 pro mille.

It may seem surprising that these two curves overlap and are straight to about 1800 kg/cm^2, but this behavior is expected from the theoretical values of the velocities; the latter are entered on the same graph (full circles for 30°C, + in circle for 50°C). The deviations of the theoretical points are of the order of 1 per cent, and they are seen to be scattered on both sides of the respective curves. A discussion of the theoretical values is given in the next section.

The points marked B1 and B2 correspond to extrapolations to 1000 kg/cm^2 of Biquard's data* on the velocity of sound to about 600 kg/cm^2; B1 is for 16.3 ±.5°C, B2 for 9.5°C. Examination of Biquard's original paper reveals that the position of point B1 is actually uncertain owing to his widely scattered data at low pressures. This is important because, theoretically, one would expect not only B2 but also B1 to fall close to the curves shown here; such a large deviation of B1, if real, would accordingly have warranted immediate investigation.

Another result derived directly from experiment is a curve of the temperature coefficient of velocity at various pressures. For instance, from Fig. 6 we may immediately plot Fig. 6a, $\frac{1}{u}\left(\frac{\partial u}{\partial T}\right)_{40°C}$. Except for one of the points, the curve runs more smoothly than may be expected on the basis of an uncertainty of ±1 in 1000 in the values of the individual factors of this coefficient. A more remarkable feature of the curve, however, is the crossing through zero and into negative values beyond 5800 kg/cm^2 applied pressure.** It will be re-

*19, p. 135

**The point at 7000 kg/cm^2 in Fig. 6a is derived from extrapolation of the curves in Fig. 6.

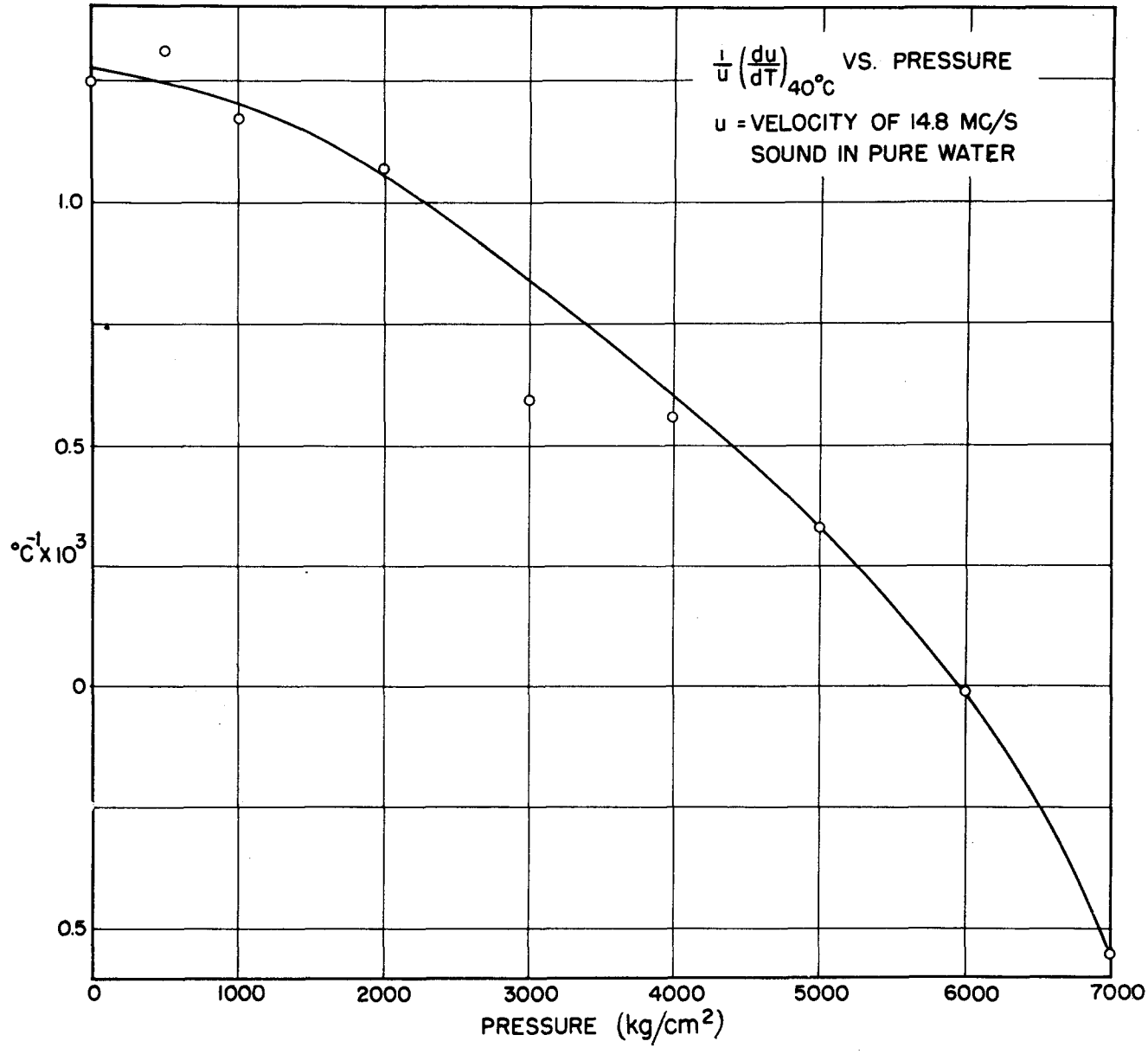
$\frac{1}{u}\left(\frac{du}{dT}\right)_{40°C}$ VS. PRESSURE
u = VELOCITY OF 14.8 MC/S SOUND IN PURE WATER
1.0
0.5
0
0.5
$°C^{-1} \times 10^{3}$
0
1000
2000
3000
4000
5000
6000
7000
PRESSURE (kg/cm²)

FIG. 6a

called that all "normal" liquids have a negative temperature coefficient of sound velocity; by this test, as by many others, water too is "normal" beyond a critical pressure range for the stated temperatures.

Besides high pressures, high temperatures also reduce the anomalies of water. As is well known,[128,154] the temperature coefficient of sound velocity does change from positive to negative around 70°C at atmospheric pressure. In the former case, as in this one, the thermodynamic explanation is that $\partial^2 p/\partial T^2$ is zero and $\partial \gamma/\partial T$ is very small in the critical range, whence $\partial u/\partial T$ must vanish.*

Theoretical Evaluation

The uses to which this type of experimental information can be put are fairly direct. From

$$u^2 = \left(\frac{\partial p}{\partial \rho}\right)_{\phi}, \qquad \gamma = -\left(\frac{\partial v}{\partial p}\right)_T \cdot \left(\frac{u}{v_s}\right)^2$$

The data for p, v, and T for water were determined by Bridgman in 1912 to five significant figures (though the published data are given for four figures only).[24] These should allow calculation of the compressibilities to at least three figures; and therefore the values of γ will be determined to a few parts in 1000 if the above equation is used together with these new velocity data.

Actually, the original p-v-T surface for water has been modified a little from time to time. The 1942 Handbook of

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*The engineering implications of this fact for delay line design are interesting (though perhaps financially prohibitive): A delay line of water at about 40°C, sealed at about 5800 kg/cm^2 pressure (and at corresponding pressures for other temperatures), should not require any elaborate thermostating, will not suffer from wavefront distortion due to temperature gradients across the line, shows no dispersion, and has effectively no attenuation. For a lower ambient temperature all these advantages can be obtained at a somewhat higher internal pressure.

Physical Constants[61] shows an average deviation among different determinations of v_s at 25 degrees of about 3 in 10,000 to 3500 atmospheres, rising to about 5 in 1000 at higher pressures; the original values of compressibilities are correspondingly uncertain. Nevertheless, it is reasonable to take Bridgman's 1912 values as a reference, in order to calculate γ at various pressures and temperatures. Future corrections of v_s and $(\frac{\partial v}{\partial p})_T$ when established with certainty, can then easily be applied to the new values for γ. An example would be the newer values at some temperatures for the specific volume of water.[30] At 6000 atmospheres and 50°C, the value differs by about 2 in 1000 from the 1912 results. The difference between the new and the old compressibilities is somewhat higher and should affect the theoretical velocity to a few tenths per cent. The search for greater accuracy would probably be premature. As Bridgman has stated, "a great deal more work would be necessary before the p-T-v surface of water is known with an accuracy corresponding to the accuracy of our knowledge of volume as a function of temperature at atmospheric pressure."* The new values of γ, and all pertinent data leading to these values, are tabulated in Table VII. Specific volumes, compressibilities and specific heats are derived from Reference (24). The values of $(\frac{u}{u_{atm}})_{theor}$ are calculated from these statically determined values and were plotted in Fig. 6. They may be compared with $(\frac{u}{u_{atm}})_{exp}$ from these experiments. The equipment and the conditions during the run were chosen so as to minimize all errors during the velocity measurements, as previously explained; therefore the raw data for velocity needed only a correction for the change in length of sonic path with pressure owing to shrinkage of the steel spacers. This correction amounts to less than 4 in 1000 at our highest pressures, wherefore the compressibility of iron** was considered accurate enough for

*Ref. 61, p. 602

**Taken from P. W. Bridgman's The Physics of High Pressures, p. 160.

Table VII

Pressure kg/cm^2	v_s (cm^3) 30°C	v_s (cm^3) 50°C	$(\frac{\partial v}{\partial p})_T$ (cm/gm) x10^{-10} 30°C	$(\frac{\partial v}{\partial p})_T$ (cm/gm) x10^{-10} 50°C	γ_{theor} ±0.02 30°C	γ_{theor} ±0.02 50°C	$(\frac{u}{u_{atm}})_{theor}$ 30°C	$(\frac{u}{u_{atm}})_{theor}$ 50°C
1	1.0041	1.0018	442±1	438±1	1.01_3	1.036	(1.000)	(1.000)
500	.9837	.9916	373_5	371	1.02_1	1.04_8	1.07	1.07
1000	.9663	.9743	330	329	1.02_7	1.05_2	1.12_1	1.11_8
2000	.9364	.9445	264	264_5	1.04_4	1.06	1.22_4	1.21_5
3000	.9105	.9205	222_5	223	1.07_2	1.05	1.31_3	1.28_3
4000	.8897	.8996	190_7	192	1.06_4	1.07_5	1.38_3	1.36_8
5000	.8719	.8818	166	165	1.07_4	1.08_8	1.46	1.45_1
6000	.8654	.8662	146_4	146_3	1.07_4	1.10_5	1.54_3	1.52_5

Pressure kg/cm^2	$(\frac{u}{u_{atm}})$ exp* 30°C	$(\frac{u}{u_{atm}})$ exp* 50°C	** 30°C x10^{-3}	** 50°C x10^{-3}	$(\frac{u}{u_{atm}})$ exp 30°C	$(\frac{u}{u_{atm}})$ exp 50°C	*** % 30°C	*** % 50°C
1	(1.000)	(1.000)	0	0	(1.000)	(1.000)	--	--
500	1.052	1.052	(0.2)	(0.2)	1.052	1.052	-3.42	-3.42
1000	1.104	1.104	(0.4)	(0.4)	1.104	1.104	-3.04	-2.50
2000	1.208	1.204	1.0	1.0	1.207_9	1.23_9	-2.62	-1.82
3000	1.303	1.291	1.6	1.6	1.301_4	1.289_4	-1.76	0.98
4000	1.393	1.371	2.2	2.2	1.390_8	1.368_8	+0.56	+0.06
5000	1.475	1.445	2.8	2.8	1.472_2	1.439_2	+0.84	+0.81
6000	1.555	1.512	3.6	3.5	1.551_4	1.508_5	+0.54	-1.05

*Before correction for spacer shrinkage.

**Correction due to spacer shrinkage, to be subtracted from previous column.

***Per cent correction to be applied to γ_{theor} provided v_s and $(\frac{\partial v}{\partial p})_T$ are error-free.

our purposes, though the spacers actually consisted of stainless steel. Obviously, twice the linear compression $\Delta l/l_o$ gives directly the fractional decrease of $\frac{u}{u_{atm}}$ needed for the correction at any pressure and temperature.

Since our equipment had not been designed for absolute velocity measurements, it was logical to calculate, instead of u itself, the ratio $\frac{u}{u_{atm}}$ at increasing pressures. The values of u_{atm} at the various temperatures, needed for the determination of corresponding absolute γ-values, might therefore be taken from independent absolute measurements.

Various published values of ultrasonic velocities at the important temperatures (30° and 50°C) and atmospheric pressure are given below. They are seen to be in poor agreement.

Table VI

Velocity in Water, in m/sec

	30°C	50°C	Comments
Schreuer (131) Seifen (132)	1509_7		Calculated from 25° data and $\partial u/\partial T$ for the range 25°-30° (= 2.5 m/sec).
Freyer (55)	1510_6		
TRE-Report (cited in (128))	(1510±1)	1544_5	30° value extrapolated
Rosenberg (128)	1500	1534	Temp. to ±1°C. Vel. to ±0.5 per cent
Hubbard-Loomis (77)	1509.9		
Willard (154) Randall (116)	1509	1543	to ±1 m/sec
Singh (135)		1545	at 50.4°

Of these, the data of Schreuer, Seifen, and the TRE Report are perhaps the most reliable.

It will be recalled that our absolute measurement of u_{atm}

by spacer-replacement confirmed Schreuer's value to 0.06 per cent. In a further experiment, relative velocities were measured in an unchanged cartridge at 30°C and 50°C at atmospheric pressure; taking Schreuer's value at 30°C as verified and correct, and including the correction for change of sonic path with temperature, the absolute velocity at 50°C was calculated to be 1548_4 m/sec.

This value differs by 2.5 parts in 1000 from the velocity given in the TRE report at 50°C. In the absence of better data for the absolute value, this is thought to be as satisfactory as could be expected. At any rate, the choice of our own values for u_{atm} at 30°C and 50°C seems reasonable, and any future adjustment of these values, like those of v_s and $(\frac{\partial v}{\partial p})_T$, can be directly applied to new corrections of γ. Apart from those uncertainties, the final values of γ of water at pressures to 6000 kg/cm^2 have an accuracy to within 0.3 per cent (owing to the 0.1 per cent deviation of the velocity data, and including 0.1 per cent for accuracy lost in occasional use of a 12-inch slide rule when the mechanical calculator was not available).

Since one of the claims of the multiple-echo method is its superiority in determining certain thermodynamic coefficients, we should compare this last result for γ with the usual derivation of γ from static experiments. It is well known that such an evaluation of specific heats requires a knowledge of the p-v-T surface accurate enough to give meaningful <u>second</u> derivatives of specific volumes with respect to temperature. Furthermore, the first function directly obtained is not C_p itself, but

$$(\frac{\partial C_p}{\partial p})_T = -T(\frac{\partial^2 v}{\partial T^2})_p$$

The values of C_p at various pressures are obtained by integration, using independently determined results of C_p as a function of temperature at any one (say, atmospheric) pressure. As a second step toward finding γ, one may turn to the relation

$$C_p - C_v = -T \frac{(\frac{\partial v}{\partial T})_p^2}{(\frac{\partial v}{\partial p})_T}$$

The expected error in the value of C_p/C_v finally obtained may be ten times the error in γ as determined by sound velocity measurements.* In this light the old values of C_p and C_v derived from the 1912 paper[24] are astonishingly good, for they give ratios that deviate on the average only about 2 per cent from the new corrected γ. This incidentally represents a nice compliment to the skill of the experimenter of 35 years ago!

Other uses for sound velocity measurements offer themselves immediately. The adiabatic and isothermal compressibilities may be compared; or, from the last equations, C_p and C_v may be determined separately by

$$C_p = -T \frac{(\frac{\partial v}{\partial T})_p^2}{(\frac{\partial v}{\partial p})_T + (\frac{v_s}{u})^2}$$

In effect, the immediate availability from sound experiments of the adiabatic compressibility and of γ permits a series of cross-checks among coefficients derived from the p-v-T surface. It may even be hoped that if <u>absolute</u> velocity data can be established to 0.1 per cent or better (perhaps with a cartridge of new design currently being constructed), it will become possible to amend the published four-figure p-v-T values themselves.

It may be questioned at this point whether it is valid at all to compare statically and dynamically derived specific heat ratios; the answer is of course that no difference is expected

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*Reference (24), p. 333: "...it must be remembered that the absolute compressibilities given here may be in error by as much as 1 per cent at the higher pressures."
p. 335: "The agreement of the two best determinations [of $\partial v/\partial p$] at the higher pressures is about .5 per cent for the lower temperature interval from 20° to 40°, 3 per cent for the interval 40° to 60°,..."

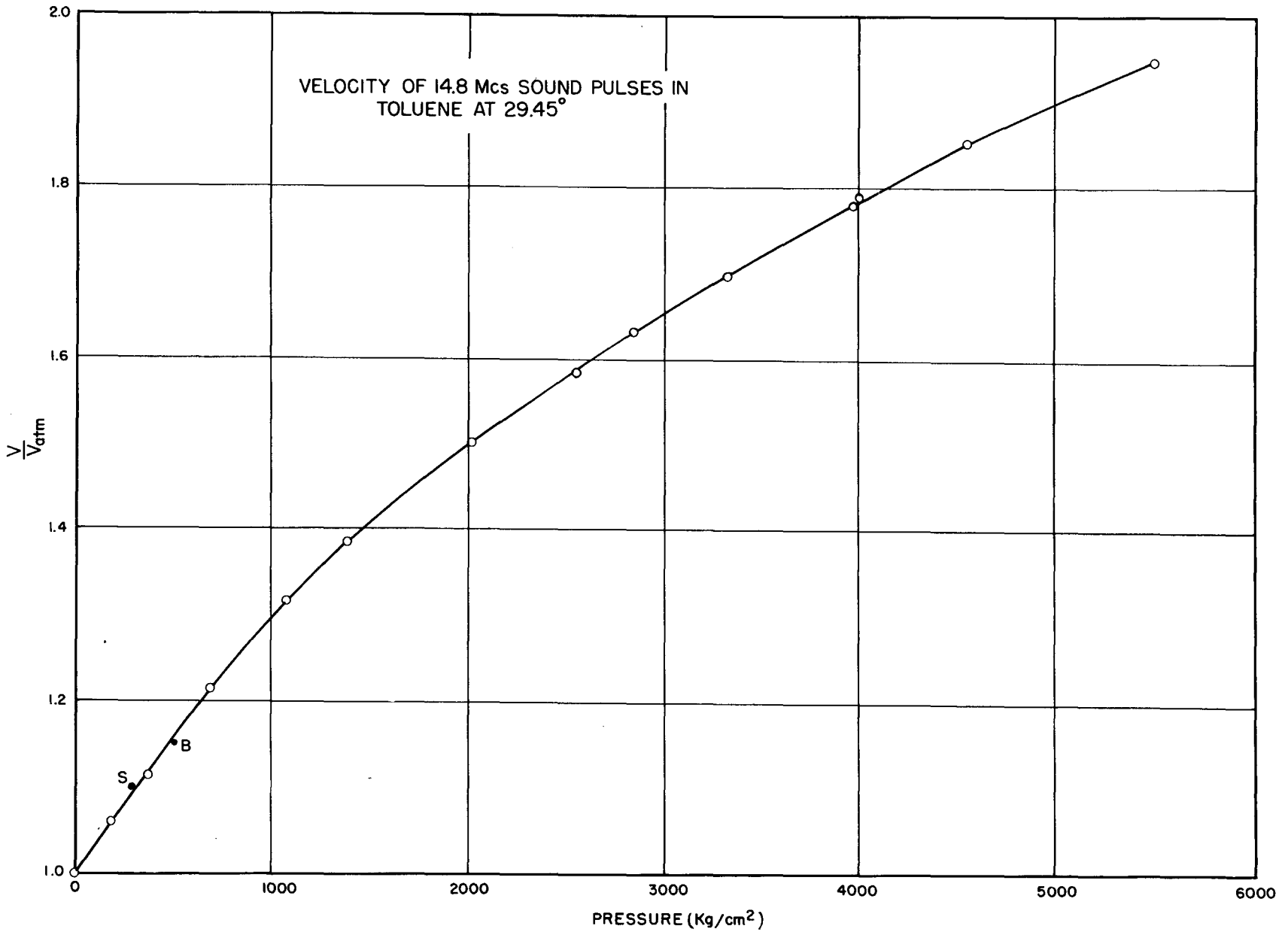
VELOCITY OF 14.8 Mcs SOUND PULSES IN
TOLUENE AT 29.45°
2.0
1.8
1.6
1.4
1.2
1.0
V/Vatm
S
B
0
1000
2000
3000
4000
5000
6000
PRESSURE (Kg/cm²)

FIG. 7

if the sound frequency is sufficiently below a dispersive region. This point will be discussed again in connection with attenuation measurements. It is sufficient to point out here that no evidence of dispersion has been found in water up to 250 Mc/s despite many different attempts throughout the past 20 years. In fact, there is evidence that no dispersion may be expected below about 10^{12} cps.[63]

For ether and toluene no dispersion is expected at or below our operating frequency. A velocity curve for toluene, a much more highly attenuating liquid than water, is shown in Fig. 7. The maximum deviation from the smooth curve is 3 in 1000 at a single point (measured during the decrease of pressure)--and this for a run in which only the first few echoes were used. The points S and B superposed on the lower part of the curve refer to results obtained by Swanson[141,142] and Biquard[19] at a lower temperature, i.e., 25 degrees and 20 degrees respectively. As in water, it is observed that the $\frac{u}{u_{atm}}$ curve starts off fairly straight, and that the slope of that line

$$u^{-1}\left(\frac{\partial u}{\partial p}\right)_{29.5^o} = 3.22 \times 10^{-10} \frac{cm^2}{dyne}$$

is not seriously affected by small temperature changes.*

Other velocity measurements, taken incidentally to supplement information on attenuation, will be described in their appropriate place.

In summary, we note that the velocity data, accurate to about 2 pro mille by the Loran method (and better than 1 pro mille using the A/R 'scope) do yield thermodynamic coefficients far more precisely than do static measurements alone. The remaining uncertainties still rest chiefly in the statically

* This is of course not necessarily true for all liquids. For ether, for instance, near 1 atmosphere, $u^{-1}(\partial u/\partial p)$ at 30°C = 7.91×10^{-10} cm^2/dyne as compared to 8.60×10^{-10} at 23.6°C(130).

derived p-v-T surfaces themselves; but any improvement there (particularly expansion to five significant figures) will, together with velocity data, result in improved thermodynamic coefficients like γ and $[(\frac{\partial V}{\partial p})_{\phi} - (\frac{\partial V}{\partial p})_{T}]$ of up to a whole significant figure more than may be hoped for without velocity data. On the other hand, there is still room for improvement in the experimental equipment (mainly the cartridge) itself in order to achieve consistent absolute measurements of velocity which are lacking in the literature.

As expected, no evidence of dispersion was discovered. In liquids like methyl acetate, however, where the relaxation frequency at ordinary pressures is fairly low, the dispersive region may be expected to move into the experimental frequency range as the pressure is increased.

VII

Attenuation Measurements - Errors

From the solution of the wave equation on page 35, we obtain

$$\alpha = (4\mu/3 + \kappa)\, \omega^2/2\rho u^3 \qquad (1)$$

where α is the attenuation constant in cm^{-1}. Following Reference (147) κ is given by

$$\kappa = 2/3\mu + \lambda \qquad (2)$$

where μ and λ are respectively the ordinary shearing viscosity and the "compression coefficient."

The necessity of retaining κ in Equation (1) instead of setting it equal to zero, as in the classical derivation of α, has been argued most forcefully by Tisza in Reference (147), but will become of interest only in the next section. In these few pages several sources of errors and other limitations on the attenuation measurements shall be pointed out before the results are discussed.

The accuracy of the measurements themselves was indicated in Table II, page 26. Perhaps with still greater care a better alignment and therefore a slightly better consistency might be achieved in some cases, particularly in the more attenuating liquids. But on the whole the table is a good representation of the present measurements. The 1/4-db uncertainty of individual readings stands for comparisons of well-shaped echoes, and is traceable to the limits imposed by the calibration and reading of the dial on the gain control.

Following the pragmatic approach used in the velocity measurements, an experimental determination by the spacer method (p.29) of the absolute value of α under the expected conditions

was tried as a check on the method itself. Using pure water at 24.5°C, the attenuation between the first and 11th echoes over a sonic path of 10 cm/echo was found to be 74.0 db. Then a 2.3-cm spacer was removed from the cartridge, and in the reduced path of 5.4 cm/echo the decrement for the first 11 echoes was redetermined to be 49.0 db. Let α_T be the error-free absolute value of attenuation (in db/cm), α_L the undetermined loss per echo by transmission, diffusion, etc., at mirror and crystal, and α_G the lumped error due to all other sources in so far as they can meaningfully be expressed in db/cm.

Therefore

$$74.0 = 100(\alpha_T + \alpha_G) + 10 \times \alpha_L$$

$$49.0 = 54(\alpha_T + \alpha_G) + 10 \times \alpha_L$$

from which $(\alpha_T + \alpha_G) = .543$ db/cm and $\alpha_L = 2$db/echo.

The value of $(\alpha_T + \alpha_G)$ in cm^{-1} divided by $f^2(sec^{-2})$ is the more conventional value used to indicate the attenuation constant; by our experiment it amounts to 2.85×10^{-16} $cm^{-1}sec^{-2}$. This is the result to compare with the standard values of α/f^2 at the same temperature to obtain an idea of the order of magnitude of α_G. Table VIII shows a summary of recent work on the absolute value of α/f^2 in water, usually at "room temperature." The agreement among different observers is seen to be relatively unsatisfactory. Comparison of the original papers makes it seem likely that the true value lies between 20 and 24×10^{-17} at 24.5°C. Fox and Rock's data seem to be the most reliable of the list at present. It would therefore seem that α_G is between 0.07 and 0.15 db/cm; the corresponding values of α/f^2 due to α_T are 24.2 to 20.1×10^{-17} $cm^{-1}sec^{-2}$. The expected value for α_G is entirely reasonable; on the one hand it is gratifyingly small compared to α_T, on the other it is of the order of the expected diffraction losses.

This preliminary result indicates that even without the use of the spacer method, meaningful results can be expected

Table VIII

Authors	$\alpha/f^2 (\times 10^{-17})$	Remarks
Teeter (145)	19 $cm^{-1}sec^{-2}$	± 20%, 25°C
Rapuano (120)	20.8	
Fox and Rock (49,51)	21.5	± 10%, 25°C, perhaps best.
Grobe (58)	22	
Pinkerton	22.5	at 25°C, interpolated
Hsu (71)	22.7	
Bär (6)	24	
Bergmann (13)	25	interpolated
Frankel (53)	26.6	
Cefola (34)	25-30	
Biquard (17)	31.5	
Willard (152)	33	± 50 %
Claeys (36)	40	
(classical value,(13))	(8)	

for the change of attenuation under changing pressures by means of multiple-echo data. The various causes for α_G and α_L are now to be examined closely, particularly as they are affected by pressure changes.

Tube Wall Losses

If for the time being we define as α_c the "classical" attenuation constant due to viscosity alone, we have

$$\alpha_c = \frac{8\pi^2 f^2}{3\rho u^3}\mu \quad cm^{-1} \tag{3}$$

by postulating $\kappa = 0$ in Equation (1). However, for propagation in tubes an additional term, α_d, owing to viscous drag along the tube walls, is to be added to α_c where

$$\alpha_d = \frac{1}{ru}\sqrt{\frac{\pi f \mu}{\rho}} \quad cm^{-1} \tag{4}$$

The radius of the tubes (r) here employed is the inside radius

of the spacers, approximately 0.6 cm. Hence α_d is for these experiments of the order of 0.01 cm^{-1} or 0.1 db/cm; the pressure-dependence of this value is small, at least in the range under investigation, since the three variables μ, u and ρ counteract one another.

Actually, the effective α_d should be much less than 0.01 cm^{-1} because: (a) the inside diameter of the spacers was intentionally made about 2 mm larger than the geometric beam, so that the "tube wall" is a sheath of quiescent liquid about 10 wavelengths thick, and not rigid steel; (b) by beam-spreading (to be accounted for separately), the affected parts of the beam fall to some extent outside the receiving transducer; and (c) clamping of the crystal reduces the amplitude of vibration at the edge of the initial wave pulse. It was one of the important results of the preliminary work at Massachusetts Institute of Technology that for <u>absolute</u> attenuation measurements by an echo method with an (uncontained) sound beam, no measurable α_d was found, even in liquids having larger viscosities;[113] the beam width and the frequency were approximately the same in both sets of experiments. Though probably of importance in high-viscosity liquids at higher pressures, and particularly at higher frequencies, α_d is not regarded as consequential in these experiments. Similar conclusions are implied in References (12), (34), (36) and (78).

<u>Conduction Losses</u>

An even less significant correction factor is that connected with energy losses by thermal conduction. The expression for conduction within the medium may be written[13] as

$$\alpha_H = \frac{2\pi^2 f^2}{\rho u^3} \left(\frac{\gamma - 1}{c_p}\right) D \quad cm^{-1} , \qquad (5)$$

in which D is the coefficient of thermal conductivity (which is less than 2×10^{-3} c.g.s. units for most liquids below 12,000 kg/cm^2). Evidently α_H is less than 1 per cent of α_L,

and therefore negligible.* Under the existing condition the effect of heat conduction on the tube walls is also negligible.

Diffraction Effects

From a strictly theoretical point of view, diffraction effects should interfere seriously with attenuation measurements, at least in that part of the beam which corresponds to the Fresnel region in the analogous optical case. The detailed analysis of V. Hughes[78] shows the various phase and amplitude distortions expected of the received pulse at the integrating receiver-crystal. But the actual results are less unfavorable; for example, in the M.I.T. experiment it was seen that the losses due to diffraction of the ultrasonic beam must be a linear function of the distance, if they are significant at all.[113] Though the distances involved in those experiments were not large (only the first echo was used), this result should hold well for the total effective path-length employed in our experiments. The experimental determination of diffraction losses for 15 Mc/s pulses traveling 20 to 60 cm in water under normal conditions yielded 0.05 db/cm.[53]

Beyond the dividing line between the Fresnel and the Fraunhofer region, the geometrical losses can be calculated more simply from the beam-spreading. However, the range at which the transition takes place is not easily fixed. Calculations on the assumption of a perfect piston source of ultrasonic waves give 50 cm from the transmitter at 15 Mc/s,[48] whereas experiments by Professor W. G. Cady[33] establish the value of about 20 cm at that frequency. The difference between experimental and theoretical beam-spreading** beyond that point

* - - - - - -
Cf. also Refs. 31, 34, 51, 81.

** No particular danger exists that the part of the pulse lost by beam-spreading will be reflected at the tube walls and picked up together with the pulse itself at the crystal. The tube walls are recessed, and are rough on the inside; furthermore, only undistorted echoes were used in these measurements.

can be enormous if the sound field is disturbed from the ideal plane-parallel case by poor crystal performance. Quinn's observations on this point have been cited on p. 17 ; other investigations into the actual sound field in front of the vibrating crystal are recorded in References 5, 13, 41 58, 67, 123, 131, 153 Each of these shows that some skepticism is justified in applying formulas derived for ideal piston sources to individual crystal vibrators, and make plausible the observed pulse distortion as well as some unpredictable geometric losses.

Nevertheless, an estimate of the order of magnitude of the diffraction losses can and ought to be made, following the arguments in the analogous optical problems.[152] Since our measurement procedure usually involves comparison of signal amplitudes of the first echo and a later one, we may calculate the relative energy densities in the geometrical beam at distances corresponding to the two echoes. The expected losses for various distances are then obtained directly in db/cm.

For the case of water at 30°C-50°C, at atmospheric pressure, and using 14.8-Mc/s sound pulses, the conclusions are (a) that beyond the first few centimeters of travel the beam loss in db/cm is fairly constant, which indicates that any echo beyond the first could be used equally well for attenuation measurements by comparison of its amplitude with the first echo; and (b) that the absolute value of this loss, about 0.04 db/cm ±30 per cent, is consistent with the measurements of α_G on p. 48, which included residual refraction and tilting effects. Though there remain several other sources of error besides the one due to diffraction, none of the others is likely to be of greater importance. Moreover, we note that the sound field is apparently not too distorted in our particular cartridge arrangement since calculations and experiments check so well.

The same favorable results apply even with varying pres-

sure, where the important parameter, the wavelength, may increase by a factor of about 1.5. The loss due to spreading does not change noticeably, but it may become more prominent in our measurements owing to the great reduction in the value of α_T at high pressures.

Our conclusion is that α_G is a relatively small factor, that a suitable correction for its presence in attenuation measurements can be made which is not seriously dependent on the exact number of echoes employed or on the changed pressure conditions. These statements imply, however, that only clearly undistorted echoes are used in the measurements, i.e., that the wavefronts do not deviate too widely from the theoretical picture which is the basis of our calculations.

Temperature Gradients

In the preliminary experiments at M.I.T. it appeared that continuous vigorous stirring of the sample under test was absolutely essential if good echo shapes and usable attenuation measurements were to be obtained. As soon as the agitation was stopped and a small thermal gradient (caused partly by the attenuation process itself) had built up across the sound field, the echo pattern became progressively more distorted by refraction effects. Similar experiences are discussed in (82) and (152). The effect is no doubt very pronounced in all research that relies on c-w methods,* and may even interfere in our method where the Loran set is used, despite very short pulses and repetition rates as low as 50 per second.

A simple calculation will illustrate the serious effects of refraction on attenuation measurements even in our method.

* - - - - - -
C. Bachem and E. Hiedman (Z. Phys. 89, 502,1934) indicate that the temperature gradient in the neighborhood of the crystal may be -100°/cm in c-w methods. One cannot help suspecting the work of Swanson, Biquard, and Willard of refraction errors on that account.

Assume the cartridge to be filled with water at 30°C and 1-atmosphere pressure. To both sides of the center line the temperature of the liquid drops evenly from T to T-ΔT at the tube walls. Since the temperature coefficient of sound velocity is negative under these conditions, the angle of deviation (θ) of the ideally plane wavefronts (radius r) from their initial direction of propagation is given by

$$\theta \cong \frac{\ell}{r} \frac{\Delta T}{u} \frac{\partial u}{\partial T} \text{ radians}$$

when the wave has traveled for ℓcm. The extent to which the initial beam, on reflection from a perfectly plane, aligned mirror, will be thrown outside the crystal disk can be gathered from a secondary experiment: 10 db attenuation of the first echo results if a perfectly aligned mirror in a 60-cm water-filled delay line without temperature gradient is tilted by 2×10^{-3} radians with respect to the transducer.* (For transducer-mirror distances of the order of 4 cm, more usual in this work, the same distance of 60-cm total sonic path would be covered by the eighth observed echo, except that the tilt of the mirror would have to be only one-eighth for the same attenuation, or 52 seconds of arc for a spurious 0.12 db/cm attenuation. In the course of 24 echoes under these conditions, the attenuation of 10 db corresponds to a mirror tilt of only 17 seconds of arc.

Using this information we note that refraction of the wavefront by 2×10^{-3} radians, in a perfectly aligned cartridge with a sonic path of 60 cm, will be accomplished by a temperature gradient of about 0.01 degree/cm, and will consequently give an additional 0.12 db/cm "attenuation." This is a discouraging result, because in our experiments such a small temperature gradient, while easily set up, is not so easily removed. Fortunately, with increasing pressures, $\partial u/\partial T$ tends to negative

*Cf. TRE-2456.

values in water, which correspondingly increases the necessary temperature gradient for the same refraction effects. In all other liquids, $\partial u/\partial T$ is negative from the beginning, so that no such losses are expected there.

This loss by refraction in water is probably responsible for much of the difficulty of making good attenuation measurements at low pressures, even though all causes for a temperature gradient have been kept to a minimum (i.e., by providing a low repetition rate and the best available thermostating). Possible remedies now being considered are inclusion of a stirring mechanism into the cartridge, and stirring by vigorous back-and-forth rotation of the whole press during runs. Apart from that, it is a source of gratification that in most of our experiments the pessimistic predictions of calculations based on simplified hypotheses did not seem to be fully borne out.

Tilting of Mirror

Very little need be added to the calculation in the foregoing section to point out the damage that a slight tilting of the mirror with respect to the transducer can do to the validity of measurements during a pressure run. Effects on the echoes of this tilting and warping, combined with those of refraction and diffraction, can be expected to account for a good deal of the observed pulse distortion, as indicated previously on pp. 33-34 , where additional causes of pulse distortion (and therefore of errors in attenuation measurements) were listed.

High-Intensity Effects

The errors introduced in velocity measurements by too large amplitudes of vibration were discussed on pp. 29 ff. Attenuation measurements are more seriously affected by high intensities in the ultrasonic beam. A measured increase of α_T by a factor of about 10 is recorded in Reference (53) when the power input into water from a pulsed 14.85 Mc/s crystal

was raised to the maximum (i.e., to an incredible 1700 watts/cm^2). Many early attenuation measurements - Sorensen's for instance -[136,137] were erroneous because this dependence of α on intensity was not realized at the time. In our multiple-echo method, it was expected that high initial intensities were necessary to secure a large number of echoes; therefore this source of error evidently merited some thought, even though there were indications that a measure of self-regulation of the beam could be depended upon. Professor Cady[33] explored a 15-Mc/s pulsed beam with a radiometer and found, "...the decay factor is abnormally large close to the crystal, but it approaches a constant value from a distance of about 3 cm on." (p. 46).

A theoretical approach to the problem did not seem fruitful. The tentative explanations[123,146] for increased attenuation of high-intensity waves involve cavitation phenomena beyond threshold intensities of the order of 3 x 10^{-2} watts/cm^2 at 1 atmosphere; but the anomalous attenuation persisted in our experiments at the highest hydrostatic pressures, a behavior inconsistent with the assumption of cavitation. Furthermore, it is extremely difficult to obtain the data on actual acoustic power input into the liquid that are essential for theoretical work on this attenuation error. At best, some estimate for maximum power input might be made from the known breaking strain of quartz crystal sections in static experiments. This strain being 1 x 10^{-3}, the maximum acoustic power developed per pulse under our conditions should be about 2 watts/cm^2. In the literature on this topic,[13,33,34,49,53,123] however, a wide range of other estimates for theoretical or actual acoustic outputs may be found.

In view of the foregoing it was thought best to prevent rather than to correct for anomalous attenuation due to high intensities. For these measurements, intensities were considered too high if the pattern of echoes as seen on the presen-

tation screen showed evidences of increased attenuation for the first few echoes as compared to later ones. As indicated in Table V, this was equivalent to using only those echoes which required a setting of the gain control of about 10.0 or higher to give them a standard height (about 0.7 inch) on the presentation unit. Echoes with higher intensities experimentally showed the described tendency toward anomalous attenuation in most liquids tested, and they were either attenuated by reduction of the plate voltage on the power stage of the driver, or neglected in these measurements.* This solution is by no means ideal, since it presupposes the use of only a few echoes in tests on liquids with a high attenuation.

Reflection Losses

The echoes used in this work suffer reflection losses at the mirror and at the crystal. In the ideal case, a plane wave at perpendicular incidence from medium 1 to medium 2 undergoes a fractional loss of energy of $1 - (Z_2-Z_1/Z_1+Z_2)^2$, where Z_1 and Z_2 are the respective acoustic impedances. For an interface between steel and water this would give a loss of sound-pressure amplitude of about 0.5 db/echo, and for an interface of nonresonant quartz and water, 2 db/echo. The second figure is not directly applicable to our case since the quartz disk supposedly has a negligible mechanical impedance to sound waves at its resonant frequency; on the other hand, the effects of clamping of the crystal, of loading with the steel backing disk, and of diffusion of sound at the unpolished crystal face, are difficult to predict. The experimental determination of the total loss per echo due to all these factors (α_L) came to about 2 db/echo (see p. 48); with other crystals under similar conditions α_L was found to be as low as 1 db/echo.

- - - - - - -

*We found interesting evidence of high intensities at greater power input into the crystal: The sputtered gold electrode was subsequently shaken off locally, and the crystal's front-face became seriously pitted.

The value and nature of α_L are such that it does not seriously interfere with the taking of measurements; that is, the loss of the pulse per echo by reflection and diffusion is not so large that it would prevent an initial pulse from setting up many echoes in a liquid with low or moderate attenuation. Furthermore, though it is necessary to be somewhat arbitrary in assigning approximately 1 db/echo as losses solely by diffuse reflection at the crystal surface in the example given, we do not expect that either this loss or the one due to transmission into quartz or steel on reflection is noticeably pressure-dependent. The change in wavelength in the range under investigation is by a factor of no more than 1.5 to 2; and the change of acoustic impedances of the three media (quartz, liquid and steel) should change the coefficient of reflection $(Z_2-Z_1/Z_1+Z_2)^2$ only slightly: Z_1/Z_2 varies with pressure from 1/30 to about 1/20 for water and steel between 1 and 6000 atmospheres.

Impurities

The effect of impurities on attenuation may be very large, and perhaps this source is most responsible for the wide variation (in some cases, by factors of 5 or more) in published values for experimentally observed attenuations under supposedly equal conditions. For example, Bazulin[9] found a 20 per cent difference in α for "pure" benzene samples supplied by different manufacturers, a difference which Kneser[89] also ascribed to very slight impurities. Willard[154] showed later that α changed by 50 per cent if a benzene sample was mixed with very small quantities of acetone. The warning of these and other examples was heeded as thoroughly as possible. At low frequencies, traces of dissolved gases may greatly influence α measurements[20] as well as velocity measurements,[144] but these effects practically disappear beyond 1 Mc/s.[58,137] Nevertheless, for safety's sake each sample of distilled water was boiled just before the measurement run.

In summary, we note that the nature and number of error

sources in attenuation experiments make such data far less reliable than the results of velocity measurements, as might be expected from published accounts of investigations of α. However, since this project inquires not about absolute, but about relative values of attenuation, the prospect for usable data is good. The preliminary spacer measurements prove that the experimental situation is not too far from the theoretical one, and that within limits correction can accordingly be applied in order to calculate relative values of α_T from measured total attenuations of the sound beam under changing pressure conditions. In fact, most error sources can either be kept small in comparison with α_T by giving proper attention to design and experimental procedure, or remain quantitatively unchanged under different pressures.

This leads to the important conclusion that (provided the mirror system does not tilt or warp with respect to the crystal) the same correction that has to be applied to the experimental value of total attenuation per echo at the outset of a pressure run will apply without important changes throughout the pressure range. This is essential to the success of the method, because, as has been shown, it would be exceedingly difficult to account quantitatively, at every new pressure, for each of the significant sources of error. The pressure-dependence of the various factors discussed is so small that they are believed to contribute less than 0.05 db/cm uncertainty in the individual values of $\frac{\alpha}{\alpha_{atm}}$ in measurements like those on water to 6000 kg/cm^2. To this uncertainty has to be added that due to the probable error of 1/4 db in individual settings of the gain control. Actually both of these errors are probably less than the spurious attenuation brought on by progressive tilting and warping of the mirror (though these cannot go too far before they are discovered and so annul that particular measurement run). Whether or not any runs could be made in the presence of this threat remained a question to be answered solely by experiment. The final demonstration of repeatability of the data within close limits was the hoped-for positive answer.

VIII

Attenuation Measurements - Results

Experimental Results for Ether, Water and Toluene

Water has the lowest attenuation of all liquids at ordinary pressures and temperatures;[13,152] it has a positive temperature coefficient of velocity, and in other respects is anomalous at the lower pressures. It is consequently one of the most difficult liquids as far as attenuation measurements are concerned. We accordingly made some short preliminary runs with a more promising liquid, ethyl ether. Figure 8 indicates the results. (The point marked 'S' indicates Swanson's[141] result for the velocity of ether at that pressure, but at a temperature lower by more than 6°C.)

The velocity data are useful to have for possible comparison of the experimental α_T and the theoretical value of the attenuation. They are also of interest at 1 atmosphere to establish the exact path-length per echo in conjunction with the known absolute velocity at that pressure and temperature. The delay between the first and eighth echoes was 479.5 μsec; the time per echo therefore was 68.5 μsec. The velocity of sound in ether at about 30°C is 949 m/sec according to Bergmann,[13] and 956 m/sec according to Willard,[152] where the data of both authors have been reduced to the same temperature using $\partial u/\partial T = -5.7$ m/sec/°C.[13] Choosing an intermediate value of 953 m/sec, the distance per echo comes to 6.53 cm at about 30°C and 1-atmosphere pressure.

The data bring out several points which were important in all attenuation measurements. The curves of attenuation are interesting only at lower pressures, after which they level off. They are expected to rise again at still higher pressures, i.e. where $\partial u/\partial p$ is small and $\partial \mu/\partial p$ is large. Also, the curves are quite well defined, with little scatter except in the low-

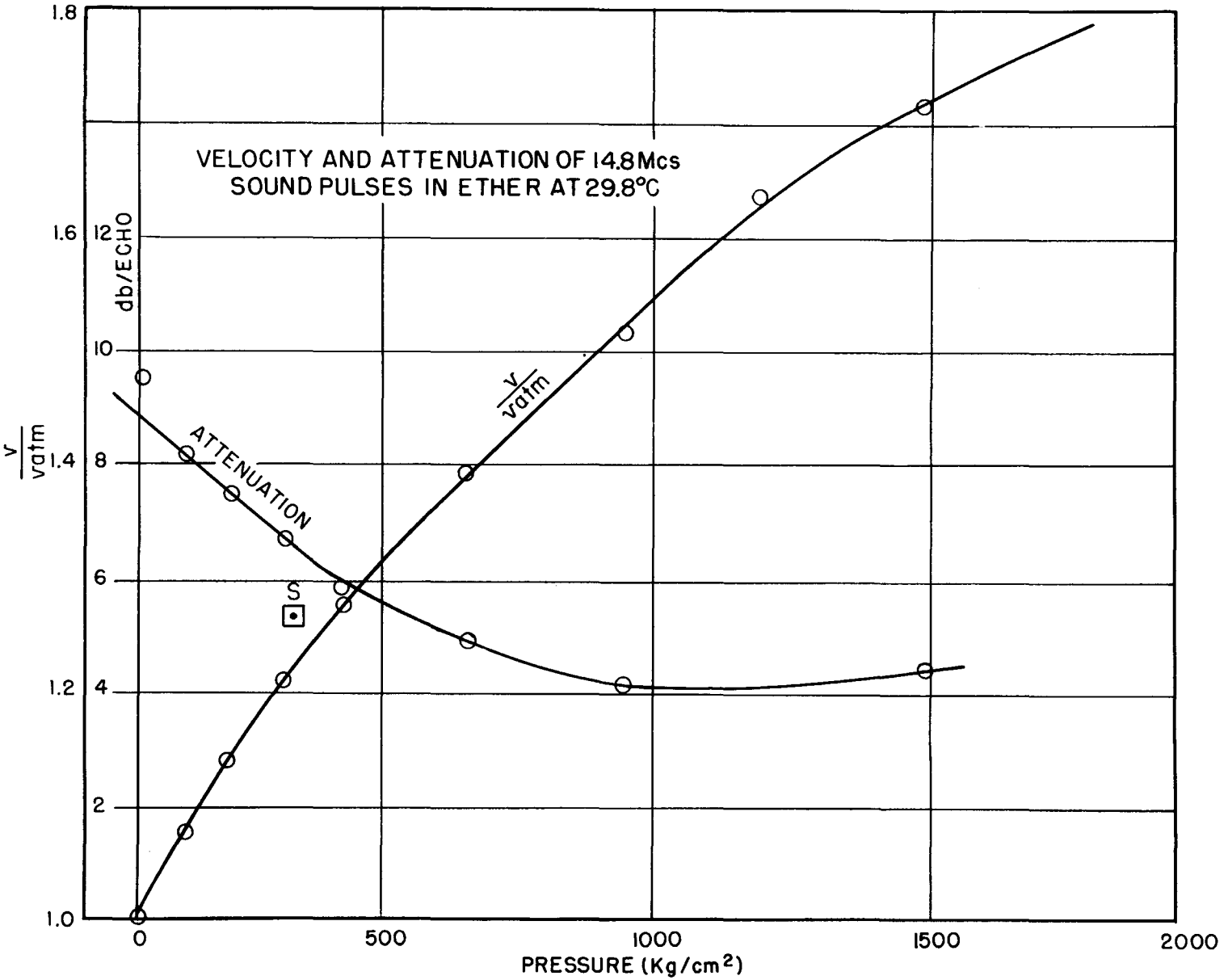
VELOCITY AND ATTENUATION OF 14.8Mcs
SOUND PULSES IN ETHER AT 29.8°C
db/ECHO
$\frac{v}{v_{atm}}$
ATTENUATION
$\frac{v}{v_{atm}}$
S
1.8
1.6
1.4
1.2
1.0
12
10
8
6
4
2
0
500
1000
1500
2000
PRESSURE (Kg/cm²)

FIG. 8

est pressure region. This was found particularly true for the curves on water where several runs were made, and is to be expected from the nature of the prominent error sources.

Another difficulty usually encountered is that of comparing our value of the total experimental attenuation, which comes to about 1.4 db/cm at the beginning of the curve, with other values independently obtained. This should establish α_T and consequently the reduction coefficients α_G and α_L by which all our experimental data are to be modified in this particular run. The following four values for α_T of ethyl ether have been published, for temperatures which are given as 23-27°C, or room temperature.

Author	Value of α_T (db/cm)	
Willard (152)	2.75	
Biquard (17)	1.08	
Teeter (145)	1.05	
Bazulin (10)	0.75	(quoted by Teeter)

The scarcity of consistent absolute values is nowhere more evident than in this list. Willard's value seems far too high, unless spectacular changes in α_T occur between his 23-27°C and our 30°C.* Teeter's value, the most recent one, is perhaps closest to the truth. It implies that the losses in our experiment, summarized by α_G, are a few tenths db/cm as expected in the absence of more marked mirror misalignment.

The best attenuation data for water under pressure are shown in Figs. 9 and 10, for temperatures between 25°C and 50°C. The curve for 25°C may be chosen to indicate the features of all data on attenuation in water. In this run, in which the most detailed precautions were taken to avoid mirror tilting and temperature gradients, there appears ample evidence

* - - - - - -

Many of the readings in this section of the paper were made during a warm three-month period when, lacking a cooling system, extended runs much below this temperature were only rarely possible or advisable.

of the repeatability of the measurements within a few tenths db/echo; furthermore, in Fig. 10 the plateau at the low-pressure end of the curve is unmistakably present,* as are the characteristic change of slope (near 2500 kg/cm^2 for this temperature) and the tendency for attenuation measurements taken during decrease of pressures to be somewhat on the low side - probably a residual refraction effect.

A significant result is implied in the two curves for 30°C (Fig. 9). The upper curve applies to attenuation per echo obtained with the first few echoes; the lower curve in this set gives the equivalent information using many echoes. The separation of the two curves is about 1/2 db throughout the range, a not unexpected value, in good agreement with the data on pp. 25-26. The interesting feature is that this difference between the curves fluctuates only by a few tenths db/echo through the whole experiment. This means that (though the lower curve is of course to be preferred) either one could be used to plot the relative change of α_T with pressure. That would involve subtracting at every point the difference between α_{exp} (as extrapolated from these data to 1 atmosphere) and α_T at 1 atmosphere and the same temperature (as taken from independent absolute measurements). Since this procedure is the one we plan to follow with these data, it is significant that the deviation in the results would be at most 1/4 db/echo at any pressure if we used the upper instead of the lower curve; for the path-length of 8.2 cm/echo in this set of data it means a maximum deviation of 0.03 db/cm in the range, and a mean deviation which is about the same as the mean deviation of each individual curve. Even with a redesigned cartridge we cannot hope for much better results. The value of 0.03 db/cm is below the estimated error resulting from the residual

- - - - - - -

*This confirms our practice of extrapolating the α-data to 1 atmosphere from data in the low-pressure region. Usually the data taken during the first hundred kg/cm^2 were much more erratic than at the higher pressures.

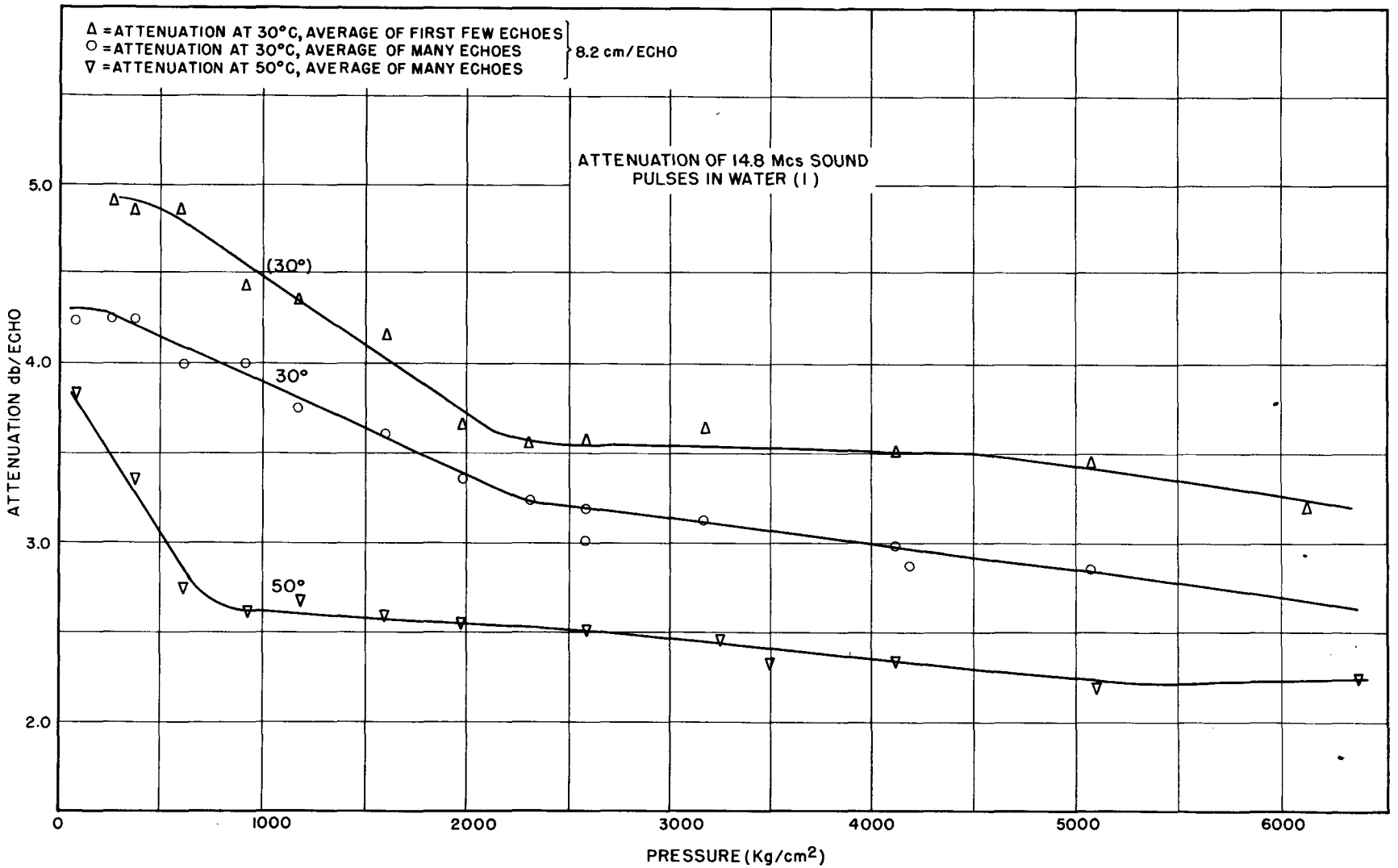
Δ =ATTENUATION AT 30°C, AVERAGE OF FIRST FEW ECHOES
○ =ATTENUATION AT 30°C, AVERAGE OF MANY ECHOES
∇ =ATTENUATION AT 50°C, AVERAGE OF MANY ECHOES
8.2 cm/ECHO
ATTENUATION OF 14.8 Mcs SOUND PULSES IN WATER (1)
(30°)
30°
50°
ATTENUATION db/ECHO
5.0
4.0
3.0
2.0
0
1000
2000
3000
4000
5000
6000
PRESSURE (Kg/cm²)

FIG. 9

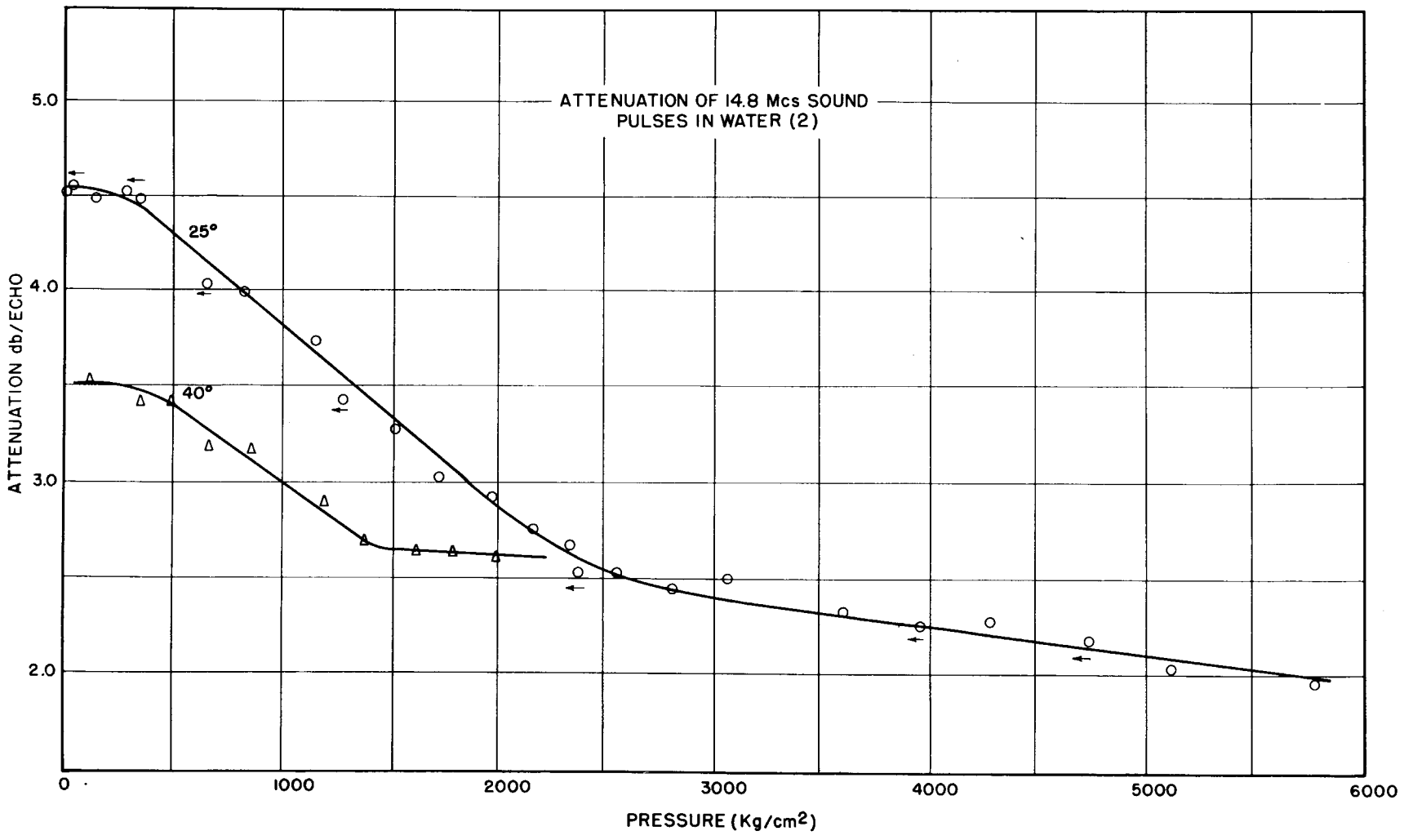
ATTENUATION OF 14.8 Mcs SOUND
PULSES IN WATER (2)
25°
40°
ATTENUATION db/ECHO
5.0
4.0
3.0
2.0
0
1000
2000
3000
4000
5000
6000
PRESSURE (Kg/cm2)

FIG. 10

pressure dependence of all normal causes operative in even the best cartridge (cf. p. 59).

It is not easy to find in the literature good absolute α_T measurements at atmospheric pressure and temperatures between 25°C and 50°C, by means of which we could translate our relative α_{exp} data into absolute values throughout the pressure range. Biquard[17] observed that $\frac{1}{\alpha}\frac{\partial\alpha}{\partial T}$ is about $0.03^{\circ}C^{-1}$ near 20°C; this was confirmed in (34) and (53). But this result applies only to a small temperature range. Baumgardt[8] claimed that between 18°C and 40°C the experimental $\frac{1}{\alpha}\frac{\partial\alpha}{\partial T}$ is equal to $\frac{1}{\alpha_c}\frac{\partial\alpha_c}{\partial T}$ from classical theory (cf. p. 49); but his absolute values for α_T are much higher than those given in most recent observations. Experiments[81,86,89,115] on other liquids, including toluene, definitely establish a nonclassical temperature coefficient there. The following tabulation shows the various available results for the coefficient of sound attenuation in water at 1 atmosphere, converted to db/cm at 14.8 Mc/s.

Temp.°C	(theoret)	Teeter (145)	F & R (51)	Baumgardt (8)
25	0.133	0.37	0.41	.564
30	0.118	0.25_2	0.39	.468
40	0.092_4	0.23_3		.388
50	0.076	0.21_2		

Teeter's values are computed from his tabulated data; although his results - the most recent available - are probably not yet the final ones, they appear to be closest to the truth. Furthermore, at present no other paper gives a complete temperature run over the desired range; therefore we shall reduce our result provisionally by means of his set of values. The table below presents the reduction for the "zero-pressure" attenuations observed in our experiments. Our values appear in the second column, before α_G and α_L have been subtracted. They are calculated by dividing the corresponding values of

the extrapolated attenuation at 1 atmosphere in db/echo, by the path-lengths per echo - which were 5.65 cm at 25°C and 40°C, 8.20 cm at 30°C and 50°C. The values for α_T are calculated on the basis of Teeter's data; α_G is considered to be about 0.1 db/cm throughout; and the α_L values that result from these assumptions are seen to have expected magnitudes (cf. pp. 48 ff.)

Temp. °C	α_{exp} db/cm	α_T db/cm	α_L db/echo
25	$.80_5$	.37	1.9
30	$.52_3$	$.25_2$	1.4
40	$.62_5$	$.23_3$	1.6_5
50	$.47_5$	$.21_7$	1.3_5

The reduced attenuation curves, based on these α_T values at 1 atmosphere, are plotted in Fig. 11. After the initial plateau, each curve shows a marked decrease of attenuation until the whole set, toward 3000 kg/cm^2, has fallen to very low α_T values within a range of 0.05 db/cm.

But perhaps the most interesting feature of Fig. 11 is the fairly regular spacing between the "knees" for the four temperatures. In fact, a simple linear law suggests itself for this shift with temperature. In the temperature range under discussion, the "critical" pressure in kg/cm^2, P_c, is numerically given by $P_c = 4400-72T$, where T is in °C. Of greater theoretical interest is another, equivalent formulation: the difference between the specific volume v_o at T°C and 1 kg/cm^2 and v_c at the same temperature and critical pressure may be called Δv; then, numerically,

$$\Delta v = 0.138 - 2.15 \times 10^{-3}T$$

within $\pm 2 \times 10^{-3}$ in the 25°- 50°C range in water. Therefore we expect Δv to become very small near 65°C. In the next section it will appear that this is in accordance with a theoret-

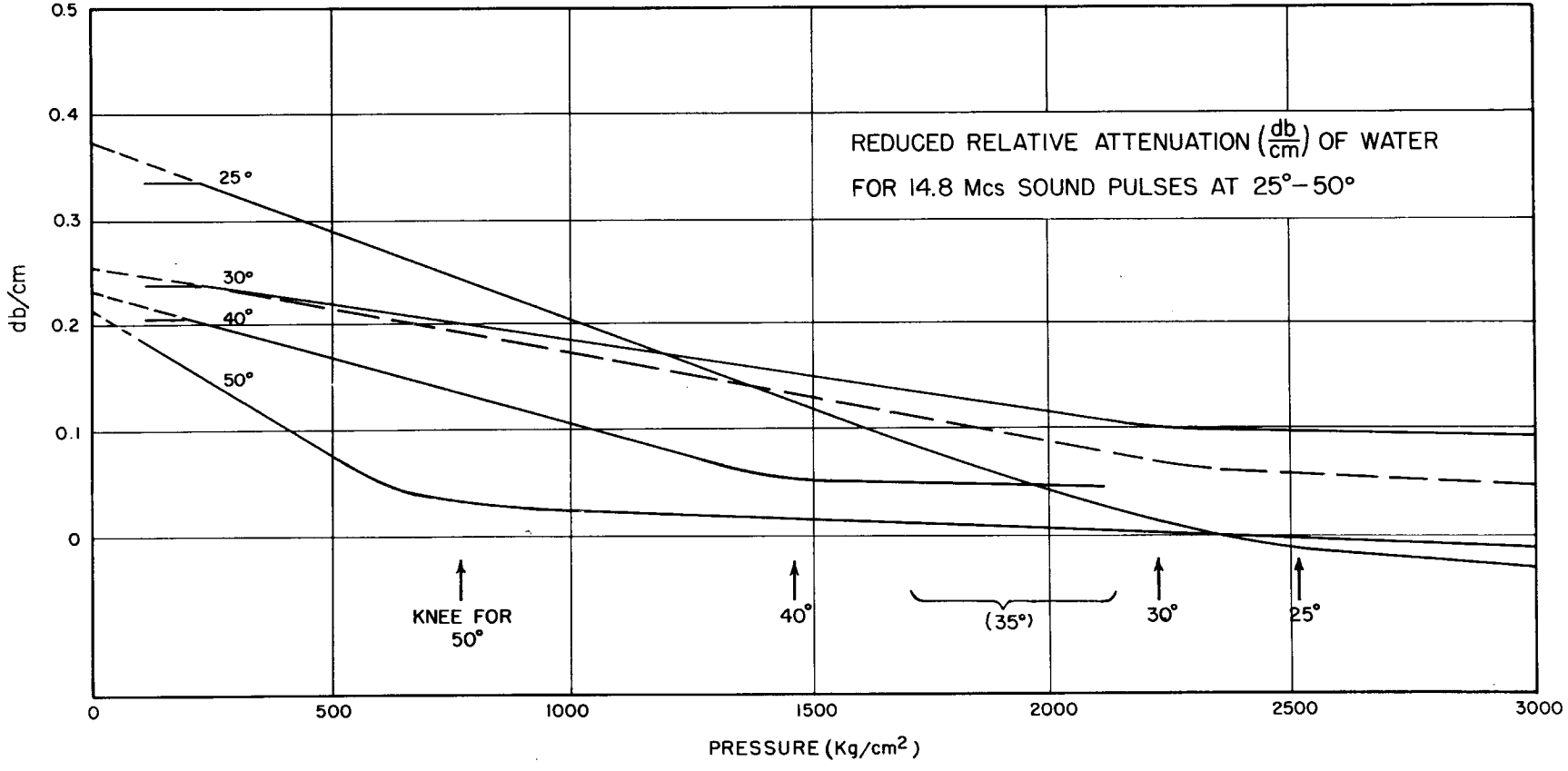
REDUCED RELATIVE ATTENUATION (db/cm) OF WATER
FOR 14.8 Mcs SOUND PULSES AT 25°–50°
25°
30°
40°
50°
db/cm
0.5
0.4
0.3
0.2
0.1
0
KNEE FOR 50°
40°
(35°)
30°
25°
0
500
1000
1500
2000
2500
3000
PRESSURE (Kg/cm²)

FIG. 11

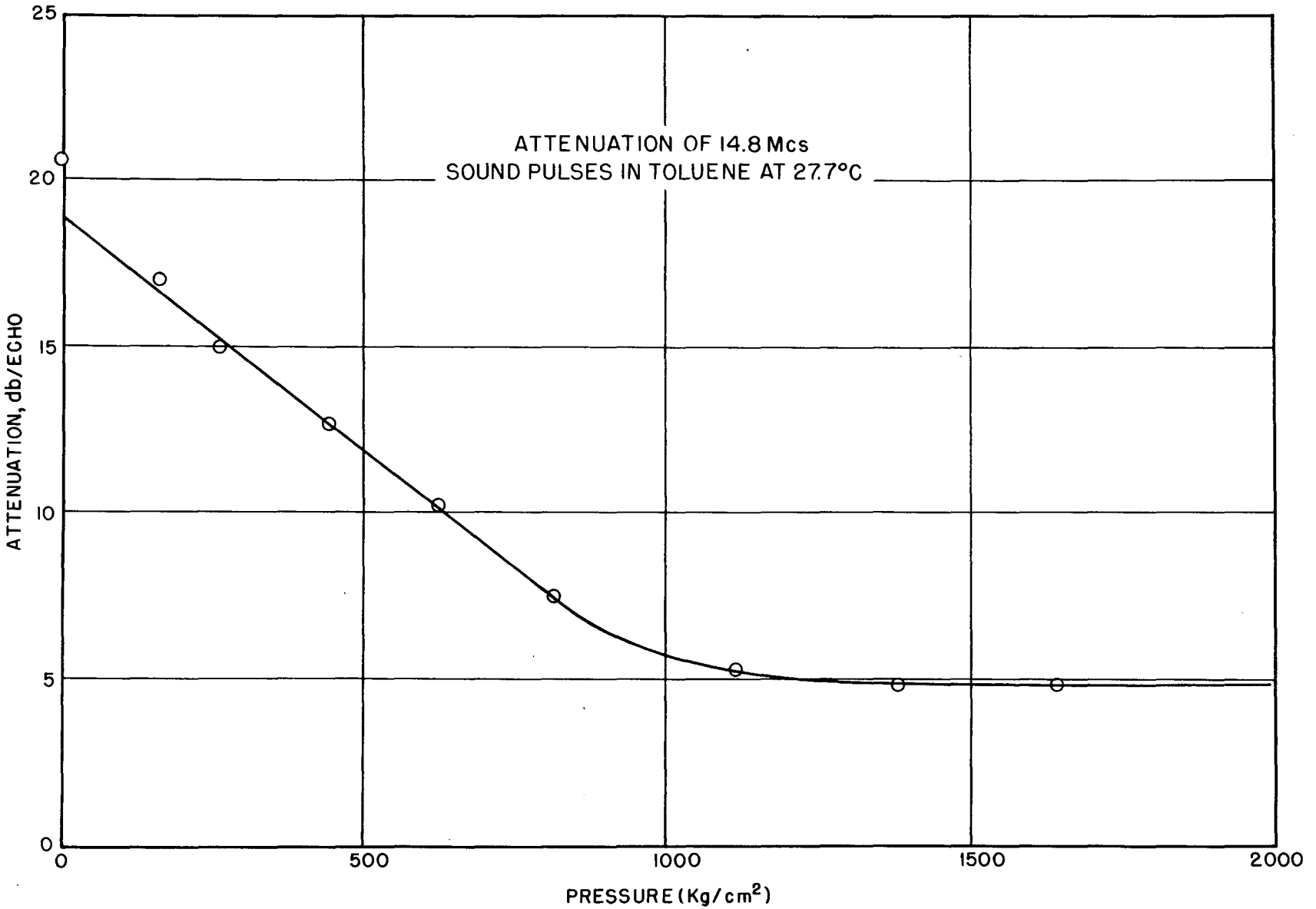
ATTENUATION OF 14.8 Mcs
SOUND PULSES IN TOLUENE AT 27.7°C
ATTENUATION, db/ECHO
PRESSURE (Kg/cm²)
0
5
10
15
20
25
0
500
1000
1500
2000

FIG. 12

ical interpretation of the anomalous break, or knee, in the α_T curves.

Figure 12 shows that the same sudden change of slope appearing in the attenuation curves for ether and water is also present in toluene. The attenuation of toluene at ordinary pressures and temperatures is between that of ether and water. The interest in this liquid lies in the fact that the only previous pressure run on the attenuation of any liquid was made on toluene at 18 - 20°C by Biquard.[19] Within his range of 800 kg/cm^2 there is no deviation of his curve from a straight line. The slope of his curve and of ours differs because of the difference in temperatures.

The only absolute α_T measurements on toluene at 1 atmosphere are those shown in the following tabulations:

	α_T/f^2 cm^{-1}sec^{-1}	Remarks
Biquard[19]	80 x 10^{-17}	18 - 20°C
Parthasarathy[110]	41 x 10^{-17}	
Willard[152]	90 x 10^{-17}	23 - 27°C.

Parthasarathy's work has been adversely criticized.[81,131] Willard's value is perhaps the best of the three; the difference between his and Biquard's value is not so large as it may seem, for $\partial\alpha/\partial T$ is positive in toluene.[86,89] Using Willard's 1.72 db/cm as α_T at 1 atmosphere and 14.8 Mc/s, we may plot the "reduced" experimental curve for attenuation vs pressure. This is done in Fig. 12b, where the small circles refer to such reduced data, taken from Fig. 12 at intervals of 500 kg/cm^2.

-IX-

Attenuation Measurements - Theoretical Discussion

A brief outline may be given of theoretical interpretations that suggest themselves in connection with these attenuation data.

The experimental values of α_T at normal temperatures and pressure differ greatly from the theoretically predicted α_c, except for exceedingly viscous liquids.[81]* The ratios of α_T/α_c are about 3 for water, 10 for toluene, and 16 for ether. Figures 12a and 12b show the first evidences that the "anomaly" of the observed attenuation breaks down at higher pressures. In Fig. 12a are the reduced experimental (α_T) and the theoretical (α_c) values, both for water at 30°C. Similar curves can be drawn for other temperatures, except that the viscosity data for water needed in computing α_c are given only for 0°, 10°, 30°, and 75°C.[30] In each case the experimental curve of attenuation is seen to drop steeply with pressure until it comes close to the theoretical one, whereupon the two approach to within the error limits. This behavior is even more evident in Fig. 12b for toluene. The needed data on viscosity[19] are not available for the whole range and so no theoretical points could be indicated beyond the juncture at 1000 kg/cm^2.** For ether it appears that the curves would meet only at much higher pressures than were used here.

Until quite recently the only theories offered for the anomalously high values of observed α_T were based on the assumption of a time-lag for the conversion of translational energy in the sound-wave into rotational or vibrational energy within

*For mercury the data are conflicting; cf. Refs. 5, 13, 91,125

**Comparison with Fig. 12 will show that the break in the curve of Fig. 12b has been accentuated slightly.

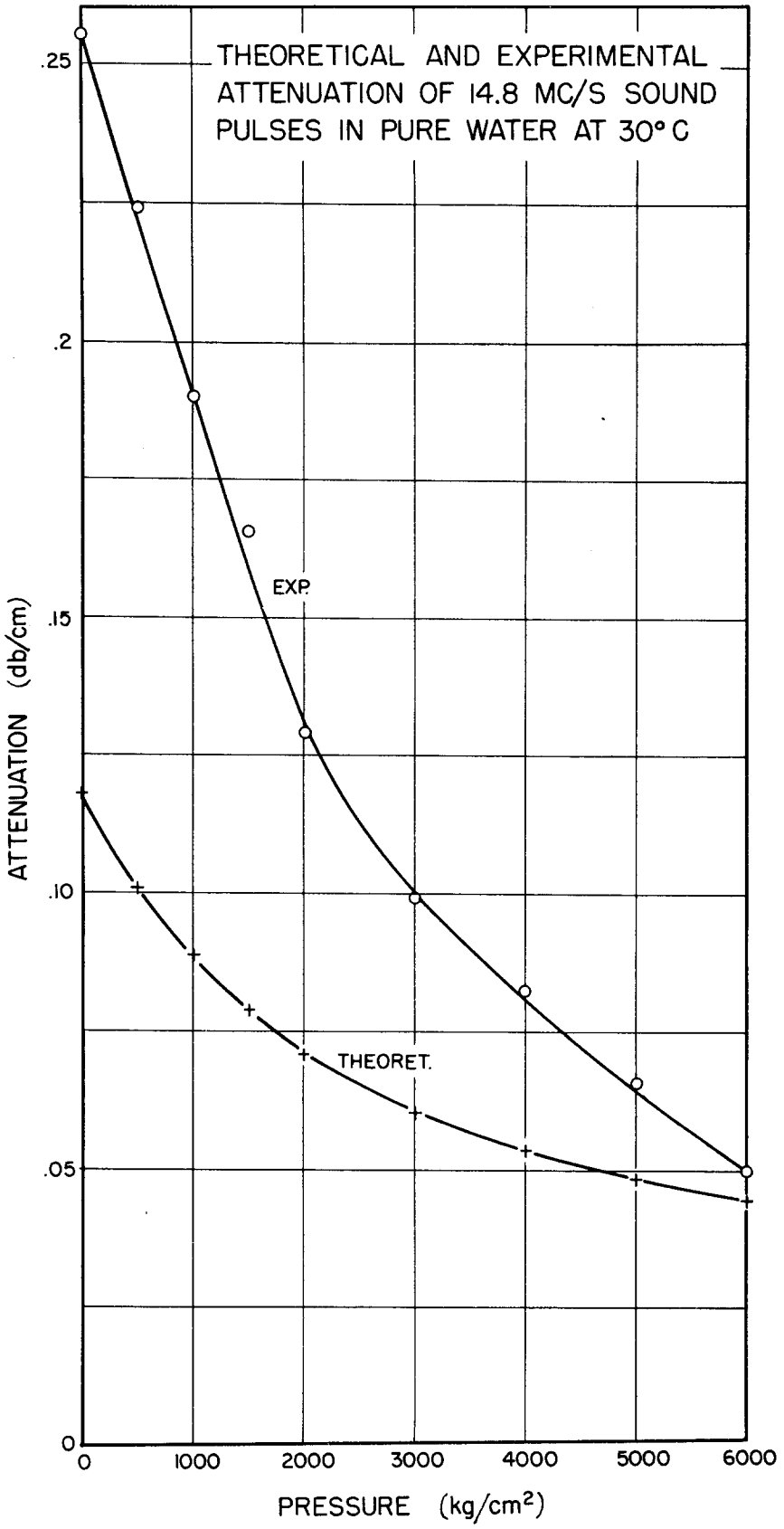
THEORETICAL AND EXPERIMENTAL ATTENUATION OF 14.8 MC/S SOUND PULSES IN PURE WATER AT 30° C
ATTENUATION (db/cm)
.25
.2
.15
.10
.05
0
EXP.
THEORET.
0
1000
2000
3000
4000
5000
6000
PRESSURE (kg/cm²)

FIG. 12 a

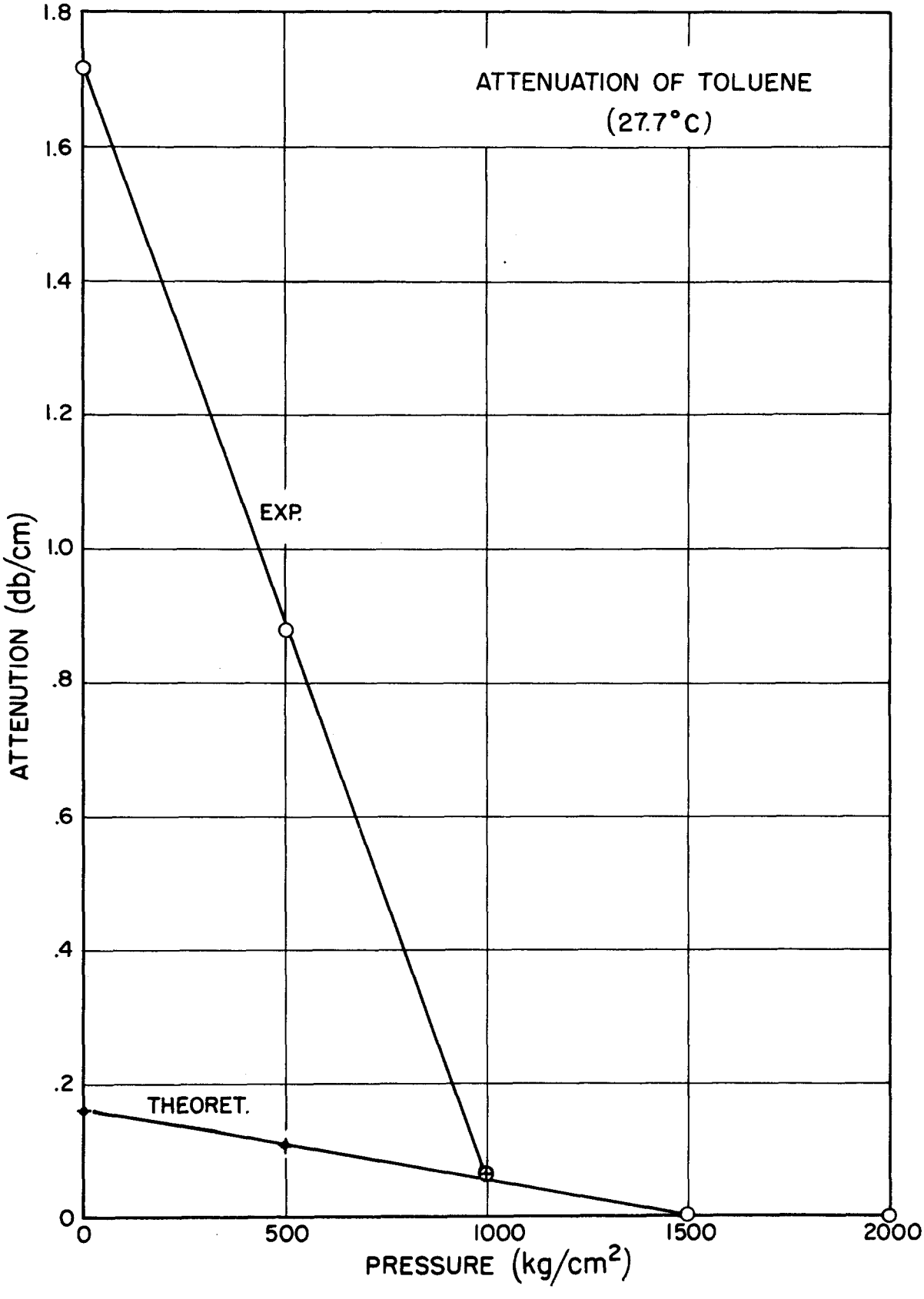
ATTENUATION OF TOLUENE
(27.7°C)
EXP.
THEORET.
ATTENUTION (db/cm)
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
0
500
1000
1500
2000
PRESSURE (kg/cm²)

FIG. 12b

the molecule. This approach has served well in some liquids like methyl acetate[6,36,89] and in the analogous case of polyatomic gases, where the relaxation frequencies of the internal degrees of freedom are of the order of the frequencies of sound waves used. However, in water, toluene and ethyl ether, as well as in most other liquids, the relaxation frequencies must be higher than 20 Mc/s, as judged from the lack of a marked dispersion of sound velocities. Particularly in water, the constancy of the velocity has for this argument been established well enough at low[21,124] and high frequencies;[63,148] hence this type of relaxation phenomenon cannot be thought to apply there.[51] The coefficient α/f^2 has been found constant from a few megacycles to 250 Mc/s.[120,145]

A thorough discussion of these points has recently been published by C. Kittel.[86] He obtains the theoretical value of an attenuation coefficient (α_r) due to relaxation phenomena within the molecule as

$$\alpha_r = \left(\frac{\pi f^2}{u}\right) \left\{ \frac{3R}{C_p^\infty} \frac{C_i}{C_v^o} \frac{f_o}{f^2 + f_o^2} \right\}$$

where C_i = specific heat of relaxing mode
C^o = low-frequency specific heat
C^∞ = high-frequency specific heat = $C^o - C_i$
f_o = relaxation frequency

At $f \ll f_o$,

$$\alpha_r = \frac{\pi f^2}{u f_o} \left(\frac{C_p - C_v}{C_p^\infty} \frac{C_i}{C_v^o} \right);$$

i.e., α_r is a constant contribution to the conventional α_c, even though f_o may be quite high. For water, α_r is of course numerically very small, because f_o is of the order of 10^{12} cps.[63] But for toluene the contribution of α_r seems to Kittell significant enough to be considered. He postulates that at about 7 Mc/s $f \ll f_o$, though the <u>positive</u> $\partial\alpha/\partial T$ observed in toluene

surely would necessitate a low f_o if "the principal part of the attenuation may be ascribed to relaxation processes."* At any rate, granted his assumption that α_r is significant at 1 atmosphere, it becomes qualitatively reasonable that with increasing pressure α_T (if $= \alpha_c + \alpha_r$) should approach the value of α_c, for as long as the pressure range is not so great as to affect the specific heats,

$$\alpha_r^{-1}\left(\frac{\partial \alpha_r}{\partial p}\right)_T = -u^{-1}\left(\frac{\partial u}{\partial p}\right)_T - f_o^{-1}\left(\frac{\partial f_o}{\partial p}\right)_T$$

The last term on the right was determined approximately on the basis of Kittel's model, even though f_o is not known, and comes to 1.2×10^{-10} $cm^2/dyne$ for toluene in the first 500 kg/cm^2 pressure. The term in u is 3×10^{-10} under the same conditions, so that $\alpha_r^{-1}(\partial \alpha_r/\partial P)_T$ should be about 4.2×10^{-10}. From Fig. 12b it can be calculated that the experimental value for the first 500 kg/cm^2 of $(\alpha_T - \alpha_c)^{-1}[\partial/\partial p(\alpha_T - \alpha_c)]$ amounts to 10×10^{-10}. The identification of $(\alpha_T - \alpha_c)$ with α_r is hardly warranted, therefore, and the excess of the observed attenuation over the classical α_c value cannot be ascribed mainly to relaxation processes of this kind, even in toluene. For our other liquids the comparison is also unfavorable; for example, for water at 30°C, the coefficient $\alpha_r^{-1}(\partial \alpha_r/\partial p)_T$ is off by a factor of 2.

So that it will not appear that Kittel's model rather than his assumption of the importance of the relaxation process within the molecule is being questioned, we may point out the good success his model has in predicting qualitatively a great number of coefficients. For example, from his development it follows that

$$u^{-1}\left(\frac{\partial u}{\partial T}\right)_p = \frac{1}{2T} - v^{-1}\left(\frac{\partial v}{\partial T}\right)_p \frac{u^{-1}\left(\frac{\partial u}{\partial p}\right)_T}{\beta_T} + (2\gamma)^{-1}\frac{\partial \gamma}{\partial T}$$

*Loc. cit., p. 14.

For water at 1 atmosphere and 40°C, both sides come to 1.3×10^{-3} within about 10 per cent. With our data for 6000 kg/cm^2, the left side of the equation is zero within the error limit of $\pm 2 \times 10^{-4}$ (cf. Fig. 6b), the right side comes to -4.6×10^{-4} -- a tolerable agreement in view of the fact that the latter figure is the small difference of two larger numbers.

In those liquids where this particular relaxation process is predominant in the experimental frequency region, data on attenuation at various pressures and temperatures will be of great interest in conjunction with Kittel's analysis. For example, in most liquids $f_o^{-1}\, \partial f_o/\partial p$ is, within generous limits, of the order of 1×10^{-10} cm^2/dyne, and $f_o^{-1}\, \partial f_o/\partial T$ should be about 10^{-2}°C^{-1}; so that we expect that an increase of 1000 kg/cm^2 of pressure should shift the relaxation frequency by about the same interval as would a 10°C rise in temperature. This could be subject to direct confirmation from the experimental α-p-T surface at a given experimental frequency. Similarly, the absolute value of f_o could be fixed by observation of maximum α_r values on the α-p-T surface, even though the fixed experimental frequency may be far from f_o at ordinary pressures and temperatures.*

Since, at least in the liquids here examined, the evidence is against holding relaxation processes within the molecule responsible for the main part of the anomalous attenuation $(\alpha_T - \alpha_c)$, two other explanations could be considered. One is that the measured attenuation contains a large contribution owing to scattering of the ultrasonic wave by density fluctuations in the liquid.[96-101] The consensus, supported by the experimental evidence, has been, however, that this process does not play a major part in attenuation experiments.[16,89,131]

The second approach neglects the scattering but retains

*If the experimental frequency were variable, one could of course obtain a very close check on the relaxation phenomena at different p and T.

an aggregation of molecules in the liquid as a fundamental assumption. This has two consequences. From a purely phenomenological point of view, the compression coefficient has to be retained in the derivation of the equation for sound (amplitude) attenuation (p. 47, Eq. 1).

It follows that $(\alpha_T - \alpha_c)/\alpha_T = 3/4\ \kappa/\mu$, which allows an experimental determination of κ as a function of pressure from our curves. Evidently $\kappa \longrightarrow 0$ at the pressures beyond the knee in the attenuation curves.

The second consequence of assuming an aggregation of molecules lies in the physical interpretation of κ.* There are two choices open. First, if the dispersion could definitely be ruled out and α/f^2 is truly constant throughout the whole frequency range, κ is real and points to a purely viscous effect without any significant relaxation effect that may be associated with the change of order during the pressure cycle. Second, κ has real and imaginary parts, which would be required if a finite relaxation time were connected with the configurational energy as suggested by Debye.[89]

The dispersion associated with order-relaxation is perhaps of a different magnitude and is certainly in a much lower frequency range than that due to intramolecular relaxation. Furthermore, there have been claims of an increase of α/f^2 for water below the megacycle range[145] which would be compatible with an order-relaxation of low f_o. Within the last two years several authors have seriously proposed that this relaxation process is responsible for the major part of the anomalous attenuation in water. Hall[60] has sketched a derivation for this contribution, α_R, from which follows

$$\frac{\alpha_R}{f^2} = \frac{2\pi^2 \beta_r}{f_o u \beta_o}$$

* - - - - - -

*Clearly, κ can be meaningfully evaluated even if the anomalous attenuation is truly a relaxation effect within the molecule (see Tisza's work, (147)); but for the reasons indicated, this is not the attenuation process in these liquids.

where β_o is the static value of the compressibility, and β_r is a relaxational compressibility. Therefore $\beta_r < 10^{-6}\beta_o$, if f_o is below 1 Mc/s. Since in general

$$\alpha_R^{-1}\left(\frac{\partial \alpha_R}{\partial p}\right)_T = -u^{-1}\left(\frac{\partial u}{\partial p}\right)_T - f_o^{-1}\left(\frac{\partial f_o}{\partial p}\right)_T - \beta_o^{-1}\left(\frac{\partial \beta_o}{\partial p}\right)_T + \beta_r\left(\frac{\partial \beta_r}{\partial p}\right)_T ,$$

we conclude that for water at 30°C, for example, the terms in f_o and β_r must add to about $+1 \times 10^{-10}$ cm^2/dynes to obtain a check between his theory and our experiments. At this time, too little information is available on the factors in f_o and β_r to attempt such a check; but it is evident that the dissociation of molecules with increasing pressure would have to be accompanied by decreasing f_o (perhaps due to the increased viscosity) if $\partial\beta_r/\partial p$ is negative as expected. A similar argument could be carried through for $\alpha_R^{-1}(\partial d_R/\partial T)_p$, except that the values of this temperature coefficient, as explained, are far from well established; -3×10^{-2} per °C for water near 25°C has been cited most frequently, and should give for the sum of the corresponding coefficients of f_o and β_r a value near -2.7×10^{-2}. This prominent difference in sign compared to the previous result for dissociation by pressure points again to the great role viscosity may play in determining f_o.

Quite apart from the question whether or not a rearrangement lag, or order-relaxation process, is involved in the attenuation process, there are two assumptions inherent in the preceding paragraphs which can be checked by comparison with other experiments: (a) the presence of molecular association at lower pressures and normal temperatures, and (b) its disappearance at higher pressures and temperatures. In this sense the experimental value of κ would indicate the amount of structure in the liquid in so far as it influences the attenuation.

These questions are most interesting in the case of water. They were raised by Professor Bridgman in 1913[25] in connection with the anomalous behavior of C_v; its initial decrease with

increasing pressures "may very possibly be an association effect."* The discussion develops the thought that initially the degree of association may increase somewhat, but would then decrease at higher pressures - "because under high pressures, when the molecules find difficulty in adapting themselves to the space at their disposal, it seems unlikely for groups of molecules to unite themselves into very close-knit units."** Even earlier*** he had postulated the decrease of the effects of "polymerization" with pressure for water. In references (26) and (27) of 1923 a most interesting indication of the large degree of association at lower pressures was given in the success of Professor Bridgman's theoretically derived formula for the thermal conductivity of eleven liquids, including water and ether;[x] the formula is based on the assumption of "more or less coherent rows" of molecules, for "it is not unnatural to suppose that the molecules tend to align themselves in this way when the intermolecular forces are allowed free play..." However, the formula breaks down if pressure is applied to the liquids, and the conclusion is that the molecules "are no longer able to take their natural arrangement."[xx]

The evidences for a large degree of association in water at ordinary pressures have since been confirmed in several ways.[42,92] The theoretical work of Bernal and Fowler[14] and the X-ray studies of Morgan and Warren[106] point to an open structure with partially satisfied tetrahedral bonding tendencies.

Dissociation increases with temperature and, as Arenberg

* - - - - - -
*Ibid, p. 104.
**Ibid, p. 112
***Ref. 23, p. 546
[x] A similarly favorable check within 10 per cent can be obtained for toluene, though this was not attempted in those references. It is of interest to note how well the formula applies to liquids not commonly considered to be associated.
[xx]Ref. 26, p. 345.

points out,[2] is completed in water below 80°C (at 1 atmosphere). This temperature region is of interest for several other reasons. The difference between α_T and α_c has decreased materially as compared to the values at lower temperatures. The value of $\partial^2 v/\partial T^2$ goes through a minimum. The velocity curve goes through a maximum around 70°C, i.e., $\partial u/\partial T$ becomes "normal" and negative even for water above this dissociation region. The temperature coefficient of compressibility also ceases to be anomalous and becomes positive just in that temperature region. Furthermore - and this is the clue that connects association of molecules with the behavior of the anomalous attenuation under pressure - this temperature is very close to the region in which we expect, on the basis of the simple linear "kneelaw" of the attenuation curves, that the anomalous part of α_T will disappear at very low applied pressures (see p. 64).

We may choose the behavior of the temperature coefficient of compressibility as an indication of the "normality" of water;[23] that is, the regions in the p-T plane in which $\partial/\partial T\ (\partial v/\partial p)$ turns from negative to positive may be correlated with the disappearance of other effects of molecular association. If that is done, we find a satisfactory correspondence between the pressures and temperatures for the knee in the attenuation curves on the one hand, and the change of sign of $\partial/\partial T\ (\partial v/\partial p)$ on the other. Because of the large number of factors that influence the course of the α-curves one should perhaps not expect too close a correlation.

Temperature °C.	Pressure* at which $\frac{\partial}{\partial T}(\frac{\partial v}{\partial p})$ becomes +. (kg/cm²)	Pressure for knee of α-curve (kg/cm²)
50°	500-1000	750 (±100)
40°	1000-3000	1500
30°	2000-4000	2200
25°	3000-5000	2600
60° - 70°	<	<(extrapol.)

* Data taken or extrapolated from Ref. (24).

The agreement is evidently better at the higher temperatures. Below 30°C the pressure at which dissociation may be thought to have been sufficiently achieved seems to be higher than the pressure at the knee of the attenuation curve, as is suggested even by a comparison of the α_T-and α_c-curves themselves in Fig. 12a.

The argument must not of course be carried beyond its limitations. The normality index here chosen is perhaps a necessary, but hardly a sufficient one.* Furthermore, $\partial/\partial T\ (\partial v/\partial p)$ is given numerically only within generous limits of accuracy, having this in common with all second derivatives of the p-T-v surface.

In summary we note that in water, which of all liquids presents probably the greatest experimental difficulties, attenuation measurements by this method yield data of considerable interest which can be tentatively correlated with structural changes in the liquid. Some lines of further research suggest themselves immediately:

1. Extension of measurements, particularly in water at low temperatures. The change of order as the subcooled region is reached should prominently determine the course of attenuation curves.

2. Extension of the frequency range of the ultrasonic beam, particularly for the study of relaxation attenuation.

3. Extension of the pressure range to include measure-

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* The use of the sign of $\partial/\partial T\ (\partial v/\partial p)$ or $\partial/\partial p\ (\partial v/\partial T)$ as normality index in water was first suggested by Bridgman, Ref.23, pp. 540 - 542. No data are available to check if the same argument can be applied to toluene. But in the case of ethyl ether it seems that the prominent change of slope in the α curve (Fig. 8) occurs in the same pressure region where $\partial/\partial T\ (\partial v/\partial p)$ becomes large and positive at 30°C (cf. Ref. 25, Fig. 25).

ments near solidification, which may entail working in different frequency ranges.

4. Redesign of the cartridge, as mentioned repeatedly in the text, particularly with a view to counteracting any internal temperature gradient.

5. In a suitably modified cartridge, extension of the method to direct experimentation on properties of the liquid which are entirely different from those discussed here. For example, thermal conductivity, thermal expansion and isothermal compression measurements can be envisaged in terms of multiple-echo data.

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